Volume 1: The Solid-Gas Singlet Delta Oxygen Generator

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The recently completed research program at the Air Force Research Laboratory, Edwards AFB Site, had as its goals for the component dealing with solid-gas generation of singlet delta oxygen: a) construction of a Raman diagnostic system for the simultaneous measurement of excited and ground state oxygen in gas-solid reactions between solid peroxides and hydrogen halides or chlorine gas, b) exploration of alternate singlet delta oxygen sources, and c) technical chemistry support to a parallel engineering effort at Boeing. This technical report summarizes the results which were obtained during this program, and a second volume will cover the results for polynitrogen research. The Appendices 2-4 contain copies of a recently awarded U.S. patent for the chemical generation of singlet delta oxygen, an article in the AFRL Technology Horizons magazine, and a journal article from Angewandte Chemie International Edition, respectively. All of the published work was done under DARPA sponsorship.

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FOREWORD

This Final technical report, entitled "The Solid-Gas Singlet Delta Oxygen Generator," presents Volume 1 of the results of a DARPA-funded study performed under JON DARPA205 by AFRL/PRSP, Edwards AFB CA. The Principal Investigator/Project Managers for the Air Force Research Laboratory were Dr. Robert Corley and Dr. Ashwani Vij.

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GLOSSARY

AFB   Air Force Base

AFRL   Air Force Research Laboratory

DARPA   Defense Advanced Research Projects Agency

EAFB   Edwards Air Force Base

IR   Infrared

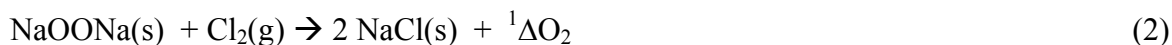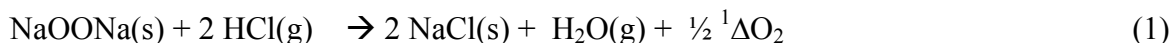OMA   Optical multichannel analyzer

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1.0 INTRODUCTION

The recently completed research program at the Air Force Research Laboratory, Edwards AFB Site, had as its goals for the component dealing with solid-gas generation of singlet delta oxygen: a) construction of a Raman diagnostic system for the simultaneous measurement of excited and ground state oxygen in gas-solid reactions between solid peroxides and hydrogen halides or chlorine gas, b) exploration of alternate singlet delta oxygen sources, and c) technical chemistry support to a parallel engineering effort at Boeing.   The following paragraphs summarize the results which were obtained during this program and a second volume will cover the results for polynitrogen research. The appendices 2-4 contain copies of a recently awarded U.S. patent for the chemical generation of singlet delta oxygen, an article in the AFRL Technology Horizons magazine, and a journal article from Angewandte Chemie International Edition, respectively. All of the published work was done under DARPA sponsorship.

2.0 REACTION CHEMISTRY

We have identified two previously unreported gas-solid reactions which produce $^1\Delta O_2$ without any external heat, light, or electrical input:

$$NaOONa(s) + 2\ HCl(g)\ \rightarrow 2\ NaCl(s) +\ H_2O(g) +\ \tfrac{1}{2}\ ^1\Delta O_2 \tag{1}$$

$$NaOONa(s)\ + Cl_2(g) \rightarrow 2\ NaCl(s)\ +\ ^1\Delta O_2 \tag{2}$$

Reactions (1) and (2), shown as ideal, balanced equations, were discovered under this DARPA program. However, the actual mechanisms which lead to the simultaneous production of ground state and singlet delta oxygen are more complex. Replacement of HCl by HBr and of Na_2O_2 by Li_2O_2 and BaO_2 in Equation (1) also produced $^1\Delta O_2$. Deuterated halide gases were also successful in generating $^1\Delta O_2$ that was detected by direct emission from the $^1\Delta \rightarrow\ ^3\Sigma$ transition at 1.27 microns.

Our investigation of the basic chemistry of these gas-solid reactions was not exhaustive but some generalities have emerged which can be correlated with spectroscopic experiments conducted in parallel. Over thirty material balances were determined by adding weighed amounts of solid sodium peroxide to ampoules contained in a nitrogen atmosphere dry box. The ampoules which were equipped with Teflon stopcocks were then connected to a vacuum line that permitted the precise addition of hydrogen chloride or chlorine gas. After the gas-solid reactions were complete, the residual solids were weighed and the liberated oxygen and unreacted HCl or Cl_2 were measured. Powdered samples as well as whole and ground beads of sodium peroxide were used. Infrared analysis of the powder and ground bead samples revealed no differences. Table 1 summarizes these material balance experiments and Equations (1) and (2) were used for stoichiometry calculations. The total oxygen yields reported in column 2 of Table 1 are based upon the appropriate limiting reagent in each case. The amount of water (5 weight % or less) included with the reagents was in the form of water vapor added to the sodium peroxide on the vacuum line.

Table 1. Material Balance Results

REAGENTS	TOTAL OXYGEN YIELD	COMMENTS
Na_2O_2 beads/HCl/H_2O	no reaction	Excess HCL
Na_2O_2 beads/HCl/H_2O	no reaction	Excess Na_2O_2
Na_2O_2 beads/HCl	no reaction	Stoichiometric reagents
Na_2O_2 powder/HCl/H_2O	59%	Excess HCl
Na_2O_2 powder/HCl/H_2O	65%	Stoichiometric
Na_2O_2 powder/HCl/H_2O	92%	Excess Na_2O_2
Na_2O_2 beads/Cl_2/H_2O	14%	Excess Cl_2

The first two and the last entries of Table 1 show a major difference between the HCl and Cl_2 reactions with Na_2O_2 beads after water pretreatment. The beads were unreactive toward HCl regardless of excess reagent but they were slightly reactive with excess chlorine. Reactions of HCl with sodium peroxide powder which was pretreated with water showed an increase in oxygen yield as the conditions shifted from excess HCl to excess peroxide. The HCl reactions

with excess Na_2O_2 were markedly more complete with nearly theoretical total oxygen yields being obtained. All listed percentages are averages from several experiments. Dry Na_2O_2 powder was unreactive toward HCl and at least trace quantities of moisture were found to be essential for reactivity. These observations are useful in interpreting the results obtained in parallel spectroscopic experiments involving Na_2O_2 reacting with HCl or Cl_2 as described below.

3.0 SPECTROSCOPY: EXPERIMENTAL DETAILS

Although direct emission from the forbidden $^1\Delta$ to $^3\Sigma$ ground state transition is highly forbidden, this emission was readily observed at 1.27 microns during HCl, DCl, HBr, or DBr reactions with Na_2O_2, Li_2O_2, or BaO_2 and Cl_2-Na_2O_2 reactions with the use of a 0.3 meter focal length spectrograph with a 1 inch, 512 element (50x500 μm pixels) linear InGaAs photodiode array at the exit plane. The grating of the spectrograph had a groove density of 600 grooves/mm and it was blazed at 1 μm. The spectrograph dispersion was roughly 5 nm/mm and the typical range of data acquisition was from 1.20 to 1.34 microns. The array detector is responsive from 0.8 to 1.7 μm with a nearly flat quantum efficiency of 80% from 1.0 to 1.5 microns and an electronic gain of 1 A-to-D count/65 photoelectrons. This spectrograph-array detector combination is referred to as an optical multichannel analyzer (OMA).

Raman spectra were measured with a frequency doubled, Nd-YLF pulsed laser (30 mJ/pulse at 527 nm and 250 ns FWHM) as the source and an OMA detection system that consisted of a high throughput spectrometer and a 1024x256 pixel (26x26 μm) gated, intensified array. The array was configured in a one dimensional 1024x1 fashion by binning each column of 256 pixels in the vertical direction into single super pixels with software. The detector had a 40% quantum efficiency and the intensified array had an overall sensitivity of 1 A-to-D count/photoelectron. The laser was triggered from a master clock at 3 KHz and the detector intensification and gating were synchronized to this master. The schematic in Figure 1 shows the overall arrangement of both the IR emission and gated Raman detection systems. Data acquisition was initiated for both OMA systems by simultaneous computer keyboard strokes for experiments involving time-correlated IR emission and Raman detection.
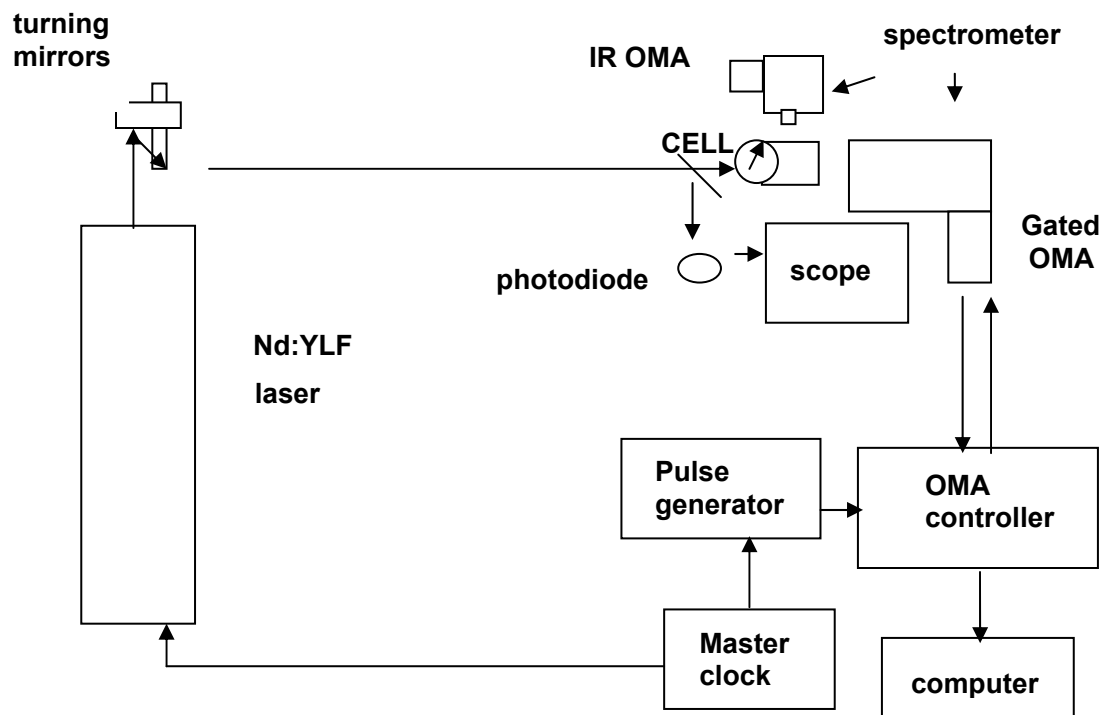
Figure 1. Spectroscopy: Hardware Arrangement

4.0 HCl-Na$_2$O$_2$ REACTION RESULTS SUMMARY

A joint AFRL-Boeing experiment conducted at EAFB produced no observable $^1\Delta O_2$ infrared signature at 1.27 microns when Na$_2$O$_2$ beads were exposed to HCl under static conditions. The behavior of powdered peroxide, however, was different. It depended upon the cell geometry which directly influences the access of HCl to solid peroxide in accordance with lines 4-6 in Table 1. The small cell (Figure 2, ~3 cm^3 volume) used originally at EAFB to observe $^1\Delta O_2$ emission offers only restricted access of HCl to solid Na$_2$O$_2$ and this results in excess Na$_2$O$_2$ conditions. This cell was used to demonstrate $^1\Delta O_2$ emission from powdered Na$_2$O$_2$ beads in the joint AFRL-Boeing experiment. When pressurized to 700 torr with HCl, large volume cells exceeding 150 cm^3 provide an excess of HCl to a typical sample of ca. 2 mmole Na$_2$O$_2$. These reaction conditions typically liberate a large blackbody IR background and a lot of heat from exothermic chemical reactions, O$_2$ amounts less than theoretical (see Table 1),

and no detectable $^1\Delta O_2$ emission in a static system. (These results seem analogous to those observed at Boeing for a flow system. Of course, a lack of detectable $^1\Delta O_2$ emission could also be due to significant $^1\Delta O_2$ production accompanied by severe quenching and an overwhelming blackbody emission. Boeing was able to completely convert Na_2O_2 samples in a flow system.) The spectroscopic cell (Figure 3) used at AFRL in static experiments for the simultaneous detection of $^1\Delta O_2$ by Raman scattering and IR emission would also qualify as a large volume cell. A dominant IR blackbody emission was generated using this cell and $^1\Delta O_2$ was not observed in emission or in Raman scattering experiments.
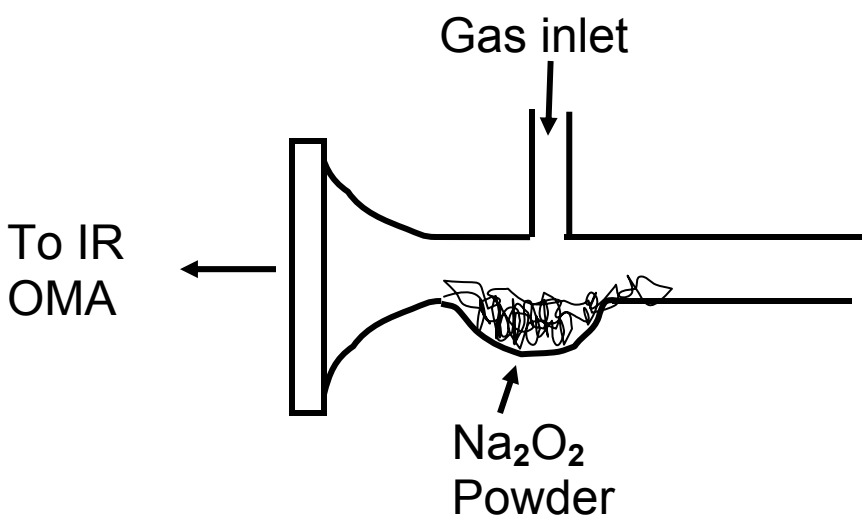
Figure 2. Original Reaction Cell

The combined results of material balance and spectroscopic experiments are consistent with Scheme 1 for an HCl-Na_2O_2 reaction that has two major reaction channels with braching ratios that depend upon whether HCl or Na_2O_2 is the excess reagent:

Scheme 1:

$NaOONa(s) + HCl(g) \rightarrow NaOOH + NaCl$ Step 1

$NaOOH + HCl \rightarrow HOOH + NaCl \rightarrow NaCl + H_2O + \frac{1}{2}\,^3\Sigma O_2$ Step 2

$HOOH$ (from Step 2) $+ 2HCl \rightarrow 2H_2O + Cl_2$ Step 3

$NaOOH + Cl_2 \rightarrow [NaOOCl] + HCl \rightarrow NaCl + HCl + ^1\Delta O_2$ Step 4
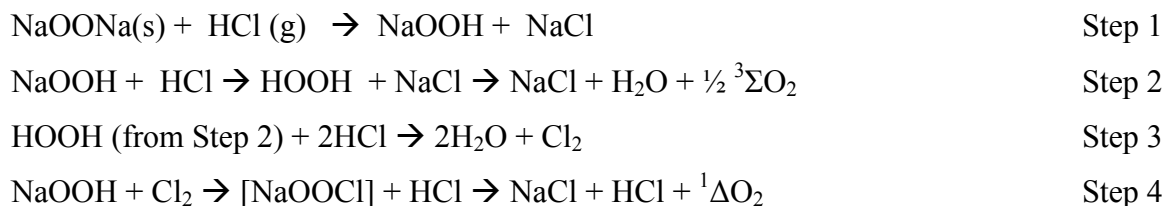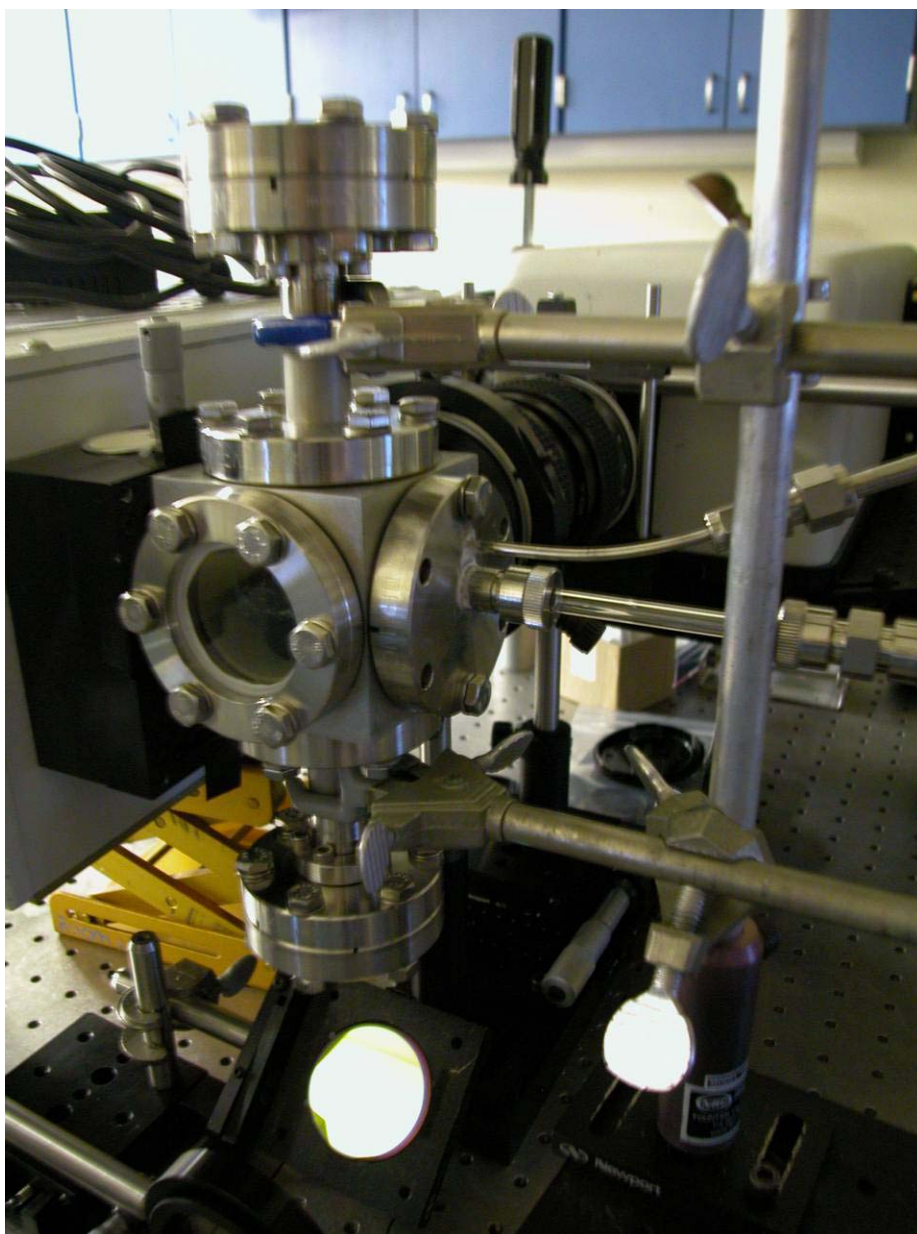
Figure 3. Large Volume Spectroscopic Cell

Under excess HCl conditions the exothermic acid-base reactions in Steps 1 and 2 convert NaOONa to H_2O_2 which undergoes thermal decomposition to $^3\Sigma$ ground state oxygen. Under excess NaOONa conditions HCl conversion of the solid peroxide to HOOH is incomplete and much less heat is generated than in the case of excess HCl. This allows the oxidation of HCl to Cl_2 by HOOH in Step 3. The reaction of NaOOH with Cl_2 in Step 4 could produce the reactive intermediate NaOOCl that is capable of liberating $^1\Delta O_2$. This highly speculative but reasonable

mechanism for the HCl- Na_2O_2 reaction is consistent with the experimental observations briefly summarized above: the production of ground state oxygen and thermal energy at high HCl concentrations and the production of $^1\Delta O_2$ with subsequent chemiluminescence at 1.27 microns rather than heat at lower HCl concentrations. The limited duration of the research program prevented a detailed, conclusive investigation of the mechanism

A point of special interest is the lack of high quality, repeatable singlet delta oxygen signature data with Raman spectroscopy when the presence of $^1\Delta O_2$ is confirmed by direct emission at 1.27 μm in static experiments. This could arise from either a very low concentration of $^1\Delta O_2$ production or a substantial production that is very efficiently deactivated by collisional and/or surface quenching. We therefore address the quantitative aspects of our ability to detect singlet oxygen and how this is affected by the gas phase quenching environment. In Appendix 1 the details are presented for the estimation of the concentration in molecules/cc of singlet delta oxygen, [$^1\Delta O_2$], from a measured direct IR emission at 1.27 microns according to Equation 3.

$$[^1\Delta O_2\ ] = \text{(Total IR counts)} / (\ \varphi_e \text{ x } 1.0 \text{x} 10^{-7} \text{ cm}^3\text{-counts/molecule)} \tag{3}$$

This relationship refers to a static experiment involving a single addition of hydrogen halide gas to a solid peroxide sample. Dividing the total integrated IR signal under the emission versus wavelength data record for the reaction period of a single HCl addition by the emission quantum yield, φ_e, and an experimentally determined apparatus constant yields the $^1\Delta O_2$ concentration. The value of the apparatus constant was estimated by Boeing to be 1.8×10^{-7} based upon the optical collection efficiency, cell volume, and detection sensitivity of the AFRL hardware. An experimentally observed value of 1.0×10^{-7} was obtained at EAFB by an independent calibration technique (see Appendix 1). The emission quantum yield (the probability of emission) is the ratio of the quenching affected excited state lifetime (τ) and the natural (τ_o) radiative lifetime and its value is calculated according to Equation (4):

$$\varphi_e = \tau/\tau_o = 1/(k_Q \tau_o) \tag{4}$$

where $k_Q = \Sigma\ k_i[i] = k_{O2}\ [O_2] + k_{HCl}\ [HCl] + k_{H2O}[H_2O] + k_{O2}*[O_2*] + 1/\ \tau_o$
and * denotes the $^1\Delta$ state of O_2.

The values of the individual $^1\Delta O_2$ bimolecular quenching constants, k_i, are available from the literature. Equations (3) and (4) explicitly account for the pressure dependence associated with the observed $^1\Delta O_2$ emission signal. This pressure dependence is necessitated by the nonradiative loss of excited state $^1\Delta O_2$ population due to collisional quenching in the gas phase. Substituting values for the bimolecular quenching constants in cc/molecule-sec and τ_o in sec:

$$k_Q = 1.5 \times 10^{-18}[O_2] + 4 \times 10^{-18}[HCl] + 4.0 \times 10^{-18}[H_2O] + 2 \times 10^{-17}[O_2*] + 1/2700 \qquad (5)$$

The joint AFRL-Boeing experiment which has been documented by Boeing is used for illustration. In this experiment approximately 300 mg of solid sodium peroxide was repeatedly exposed to HCl at a pressure of ca. 600-700 torr. The sample reacted spontaneously with each HCl addition for ca. 120 seconds. During the course of each two minute reaction the pressure typically dropped by 50 torr in accordance with Equation (1) and the reaction cell was evacuated between runs. At the beginning of each reaction the gaseous quenching environment presented to the nascent oxygen is entirely HCl (~600 torr) and Equation (5) can be approximated as:

$$k_Q \sim 4 \times 10^{-18}[HCl] + 1/2700 = (4 \times 10^{-18} \text{ cc/molec-sec})(2 \times 10^{19} \text{molec/cc}) + 3.7 \times 10^{-4} \text{ sec}^{-1} \qquad (6)$$
$$k_Q \sim 80 \text{ sec}^{-1}$$

This gives a rough value of 5×10^{-6} for φ_e that would obviously change over the course of the reaction as HCl is converted to H_2O, O_2, and $^1\Delta O_2$. The total IR emission signal recorded during a typical reaction was 1.5×10^6 counts. Substituting these values in Equation (3) gives a $^1\Delta O_2$ concentration of 3×10^{18} molecules/cc. During a reaction the 600 torr of HCl is reduced by ~ 50 torr and this corresponds to a total oxygen production of 2×10^{18} molecules/cc according to Equation (1). This approximate calculation indicates that the total oxygen production from Equation (1) is in the form of $^1\Delta O_2$ (3×10^{18} molecules/cc) and severe quenching efficiently converts it to ground state oxygen. The published $^1\Delta O_2$ quenching constants have a range of values and this calculation is solely intended to indicate that the yield of excited state O_2 ($^1\Delta O_2$ /total O_2) during the HCl-Na_2O_2 reaction is more likely tens of percent rather than a fraction of a percent.

The mechanistic complexity of the HCl-Na_2O_2 reaction is highlighted in Figure 4 where a reaction mixture shows a dark nucleus that is followed by the emission of orange- yellow light. This behavior is typical of reactions that involve the production of excited states and perhaps radical species. The misleading simplicity expressed in Equation (1) was further illustrated during an HCl-Na_2O_2 reaction that was monitored simultaneously for direct $^1\Delta O_2$ emission and Raman scattering with the arrangement in Figure 1. A cell design shown in Figure 5 was used in this case where a small gas-solid reaction region on the left is separated from a laser Raman scattering observation region by a teflon stopcock. A 600 mg sample of powdered sodium peroxide was placed in the sample reservoir and HCl gas was rapidly added to a pressure of 300 torr with the stopcock open slightly to vacuum. The rapid addition of the HCl caused some sodium peroxide to be swept into the laser beam within the Raman scattering region of the cell on the right side of Figure 5. Intense Mie scattering due to the solid particles and aerosol formation illuminated the entire laboratory with laser light. The IR emission integrated over a 10 sec period is shown in Figure 6 and a time-correlated but spatially separated series of six 2 second Raman accumulations is depicted in Figure 7. The wavenumber axis for the Raman spectra in this report was calibrated from a fit of the data points (pixel versus cm^{-1}) shown

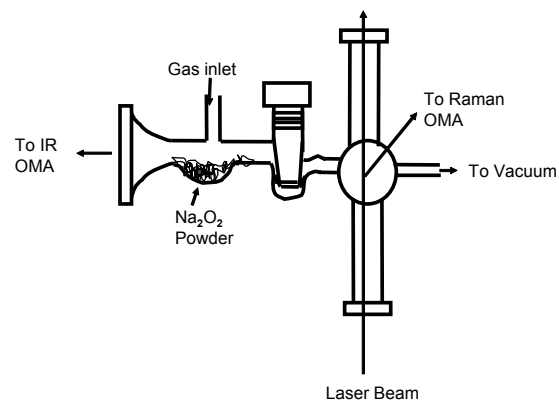**Figure 4. Visualization Of Solid Peroxide-HCl Reaction**
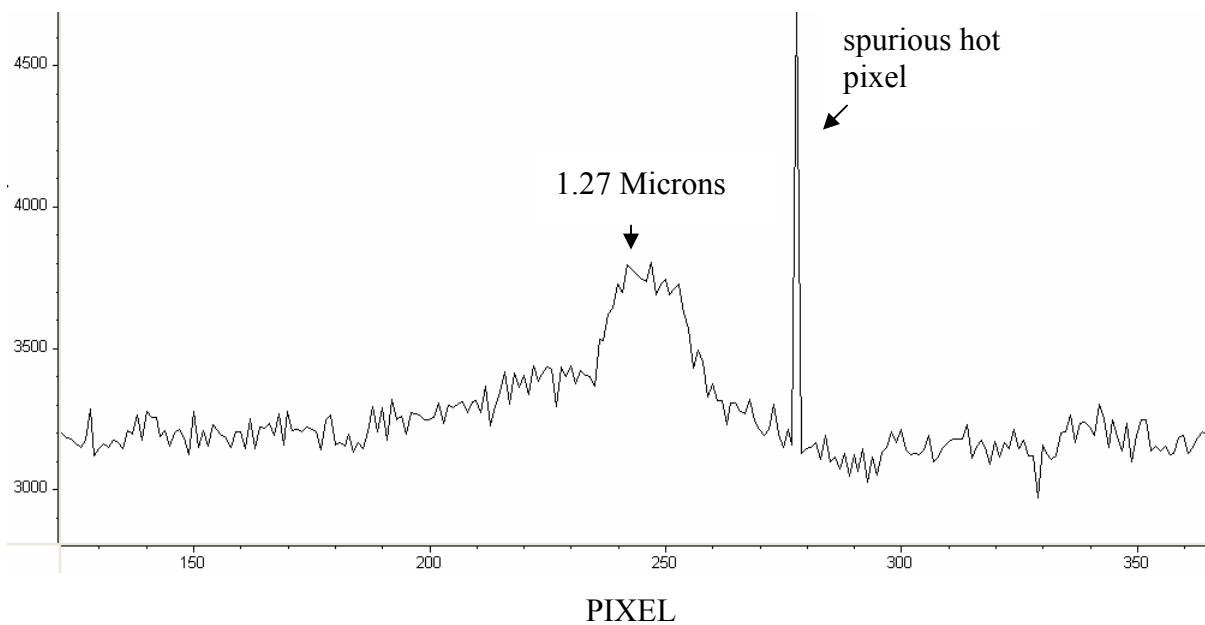
Figure 5. IR Emission-Raman Cell

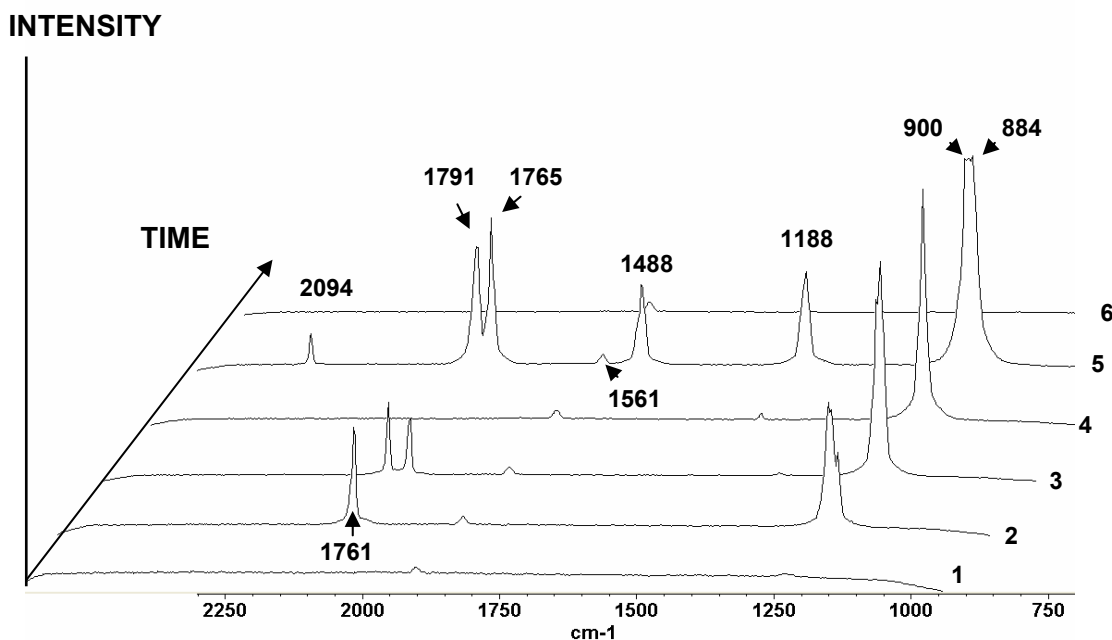**Figure 6. IR Emission from $^1\Delta O_2$ at 1.27 Microns**

Figure 7. Sequential Raman Spectra During HCl-H₂O₂ Reaction Under Flowing Conditions. (The wavelength axis is aligned with trace 5)

in Figure A-1. A constant intensity feature in all six Raman traces in Figure 7 is due to ground state oxygen at 1561 cm⁻¹ which is probably generated within the left portion of the cell and then swept into the laser beam and is related to the weak singlet delta oxygen emission in Figure 6. However, the intense feature at 1488 cm⁻¹ in Figure 7, trace 5 seems to arise from a sudden chemical event within the Raman observation region and corresponds closely to the singlet delta oxygen vibrational frequency observed at 1483 cm⁻¹ during calibration (see Appendix 1) . The other features in Figure 7 are currently unassigned but are the subject of ongoing theoretical calculation at EAFB. Additional experiments were performed to aid in identifying the various peaks in Figure 7 and to reproduce this result. The gas phase Raman spectrum from 85% hydrogen peroxide is shown in Figure 8. This spectrum corresponds to 2.8 torr of H₂O₂/H₂O with 1.3 torr of air in a flowing system and a 20 second data collection period. The 1559 cm⁻¹ peak is ground state oxygen and the peaks at 1394, 1260, and 871 cm⁻¹ are due to hydrogen peroxide.

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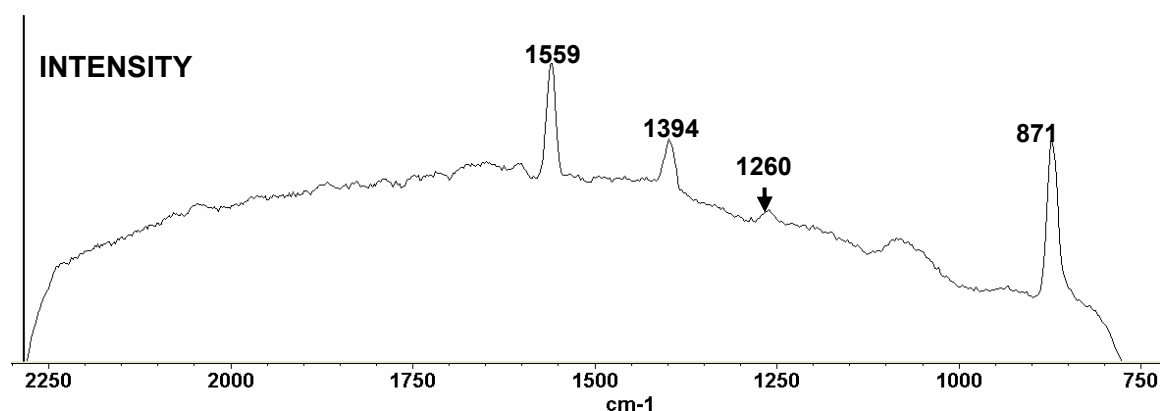
Figure 8. Raman Spectrum Of Gaseous Hydrogen Peroxide In Air

The H_2O_2 peak at 1394 cm^{-1} in Figure 8 is 94 cm^{-1} distant from the 1488 cm^{-1} feature in Figure 7 that is assigned to $^1\Delta O_2$ and this is well beyond the observed 5 cm^{-1} range of peak position variability exhibited over a wide range of experiments. (See Raman spectra in Appendix A.) A flow experiment similar to the one which produced the data in Figure 7 was performed with powdered Na_2O_2 and nitrogen gas in place of HCl and the resulting Raman spectrum appears in Figure 9. The major features at 871, 2038, and 2021 cm^{-1} do not exactly match peaks in the spectrum of Figure 7. Furthermore, the experiments with hydrogen peroxide or sodium peroxide in the absence of HCl did not give rise to the 1791,1765, 1488, and 1188 cm^{-1} features in Figure 7. Several attempts to reproduce the results for the flow experiment in Figure 7 were not successful. Nevertheless, it may be concluded that the intense feature appearing at 1488 cm^{-1} in Figure 7 could not be attributed to H_2O_2, solid Na_2O_2 , or perhaps laser photolysis products of those peroxides and singlet delta oxygen is the reasonable assignment at 1488 cm^{-1}.

INTENSITY

2038 2021   871

                                                          956

2250   2000   1750   1500   1250   1000   750
                                        cm-1
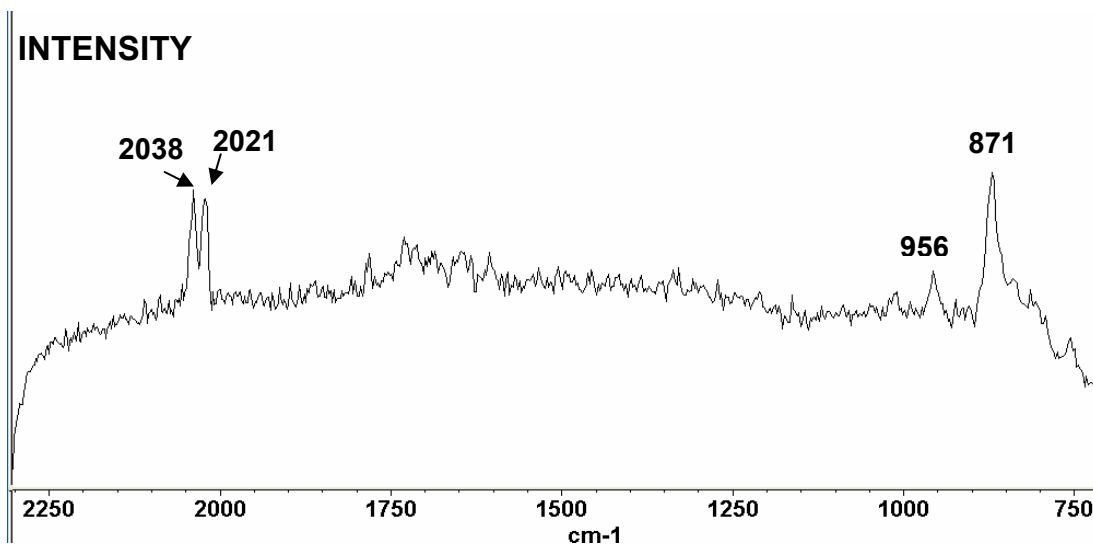
Figure 9. Raman Spectrum Of Sodium Peroxide Powder Suspended In Nitrogen

5.0 Cl_2-Na_2O_2 REACTION RESULTS SUMMARY

The Cl_2-Na_2O_2 reaction was also spectroscopically investigated. $^1\Delta O_2$ emission at 1.27 microns was readily observed during a 5 second integration (See Figure 10). The reaction took place with the cell represented in Figure 5 slightly open to vacuum after 300 torr of chlorine were added to ca. 500 mg of powdered sodium peroxide. The Raman spectrum correlated with Figure 10 indicates ground state oxygen only (see Figure 11). Additional experiments indicated that unassigned features along the baseline are due to impurities in the chlorine. A weak Raman signature due to $^1\Delta O_2$ at 1488-1483 cm^{-1} could be masked under this baseline.
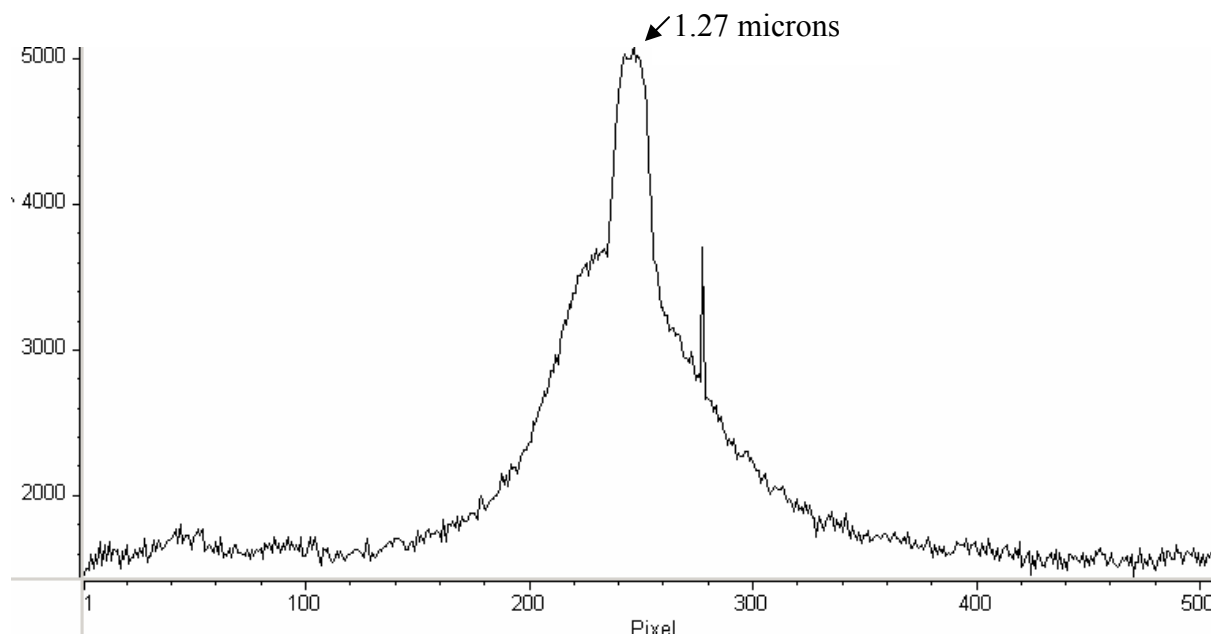
Figure 10. IR Emission from $^1\Delta O_2$ at 1.27 Microns

The spectroscopy experiments and the averaged material balance results in the last line of Table 1 permit some conclusions about the Cl_2-Na_2O_2 chemistry. When Na_2O_2 beads are treated with water vapor for the material balance experiments a surface reaction to produce hydrogen peroxide and sodium hydroxide results. Subsequent addition of Cl_2 produces $^1\Delta O_2$. This is essentially the conventional basic hydrogen peroxide reaction occurring on the bead surface.

Scheme 2:

$NaOONa_{(s)} + 2HOH_{(g)} \rightarrow H_2O_{2(l)} + 2\ NaOH_{(s)}$

$2NaOH_{(s)} + H_2O_{2(l)} + Cl_{2(g)} \rightarrow\ ^1\Delta O_{2\ (g)} + 2H_2O_{(g)} + 2\ NaCl_{(s)}$
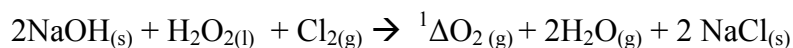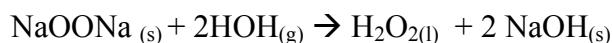
This reaction is believed to involve the $ClOO^-$ ion as an unstable intermediate that decompose spontaneously to give $^1\Delta O_2$ and chloride ion. In our experiments a possible mechanism is as follows:

Scheme 3:

$NaOONa + HOH \rightarrow NaOOH + NaOH$

$Cl_2 + NaOOH \rightarrow [NaOOCl\ ] + HCl$

$[NaOOCl] \rightarrow NaCl +\ ^1\Delta O_2$

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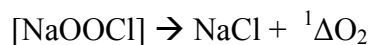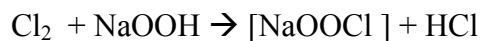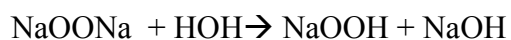
In powdered Na_2O_2-Cl_2 reactions such as the one responsible for Figures 10 and 11, water was not intentionally introduced but Na_2O_2 was handled in the open air. This proposed mechanism is also speculative. However, some definite conclusions are possible based upon the combined chlorine and HCl reactions with sodium peroxide.
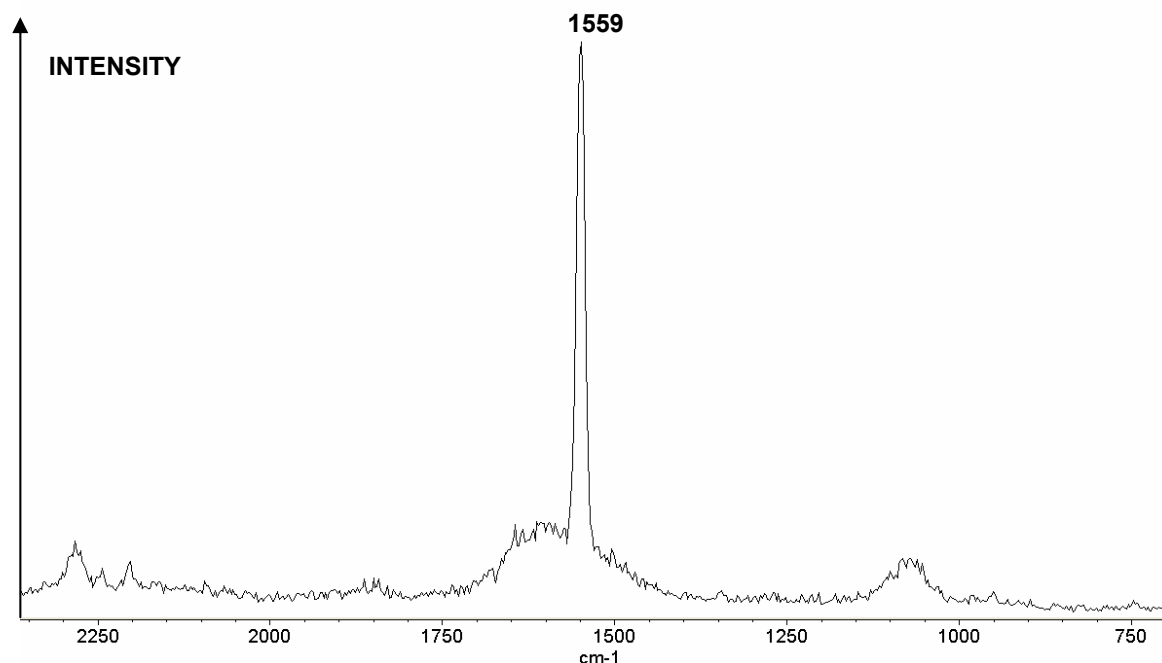
Figure 11. Raman Spectrum During Cl_2-H_2O_2 Reaction Under Flowing Conditions

6.0 CONCLUSIONS

a) The Cl_2-Na_2O_2 system clearly demonstrates that $^1\Delta O_2$ can be produced (Figure 10) in a gas-solid reaction without invoking liquid phase reaction chemistry. The absence of large amounts of hydrogen containing compounds in this system precludes the production of either water or hydrogen peroxide as major products.

b) The HCl-Na_2O_2 reaction produces ground state oxygen from the thermal decomposition of HOOH under excess HCl conditions. The use of less than stoichiometric amounts of HCl would favor the conversion of Na_2O_2 to solid basic peroxide which could react further with co-generated Cl_2 to liberate $^1\Delta O_2$.

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c) Solid peroxides clearly produce $^1\Delta O_2$ with both Cl_2 and HCl. (Gaseous DCl , HBr, and DBr are also effective.) The degree of quenching experienced by $^1\Delta O_2$ in a high pressure gaseous environment and perhaps on solid reactant/product surfaces has not been resolved and the $^1\Delta O_2$ yield is not well established. Our results suggest that the $^1\Delta O_2$ yield is significant in a total reaction pressure of nearly one atmosphere but the quenching is also severe.

Unresolved questions which need to be investigated in order to assess the potential of gas-solid reactions for $^1\Delta O_2$ generation for chemical lasers are:

1) What are the identities of the intermediate species leading to $^1\Delta O_2$ formation in both the HCl-Na_2O_2 and Cl_2-Na_2O_2 reactions and the associated detailed reaction mechanisms? Could unstable solid NaOOH be generated in situ from gaseous HCl and solid Na_2O_2 powder in a fluidized bed and then be reacted with Cl_2 gas to give $^1\Delta O_2$? The elimination of treacherous liquid basic hydrogen peroxide solutions and liquid phase quenching of $^1\Delta O_2$ as well as superior weight efficiencies would result. The experiment and the results summarized by Figure 7 suggest some validity to these assumptions and additional experiments along these lines are recommended.

2) What are the relative quenching effects of finely divided solid peroxide powders, alkali/alkaline earth metal halides, and HCl or chlorine on known quantities of $^1\Delta O_2$?

APPENDIX A: Absolute $^1\Delta O_2$ Measurement

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APPENDIX A: Absolute $^1\Delta O_2$ Measurement

In Figure A-1, the data used for the calibration of the wavelength axis of the Raman detection system are shown. Three separate known wavelength standards were superimposed to make this calibration: an O_2/He microwave discharge (1555 and 1483 cm^{-1}), a mercury lamp (684.6, 1665.0, and 1728.2 cm^{-1}), and a krypton lamp (1043.9 and 1964.4 cm^{-1}).
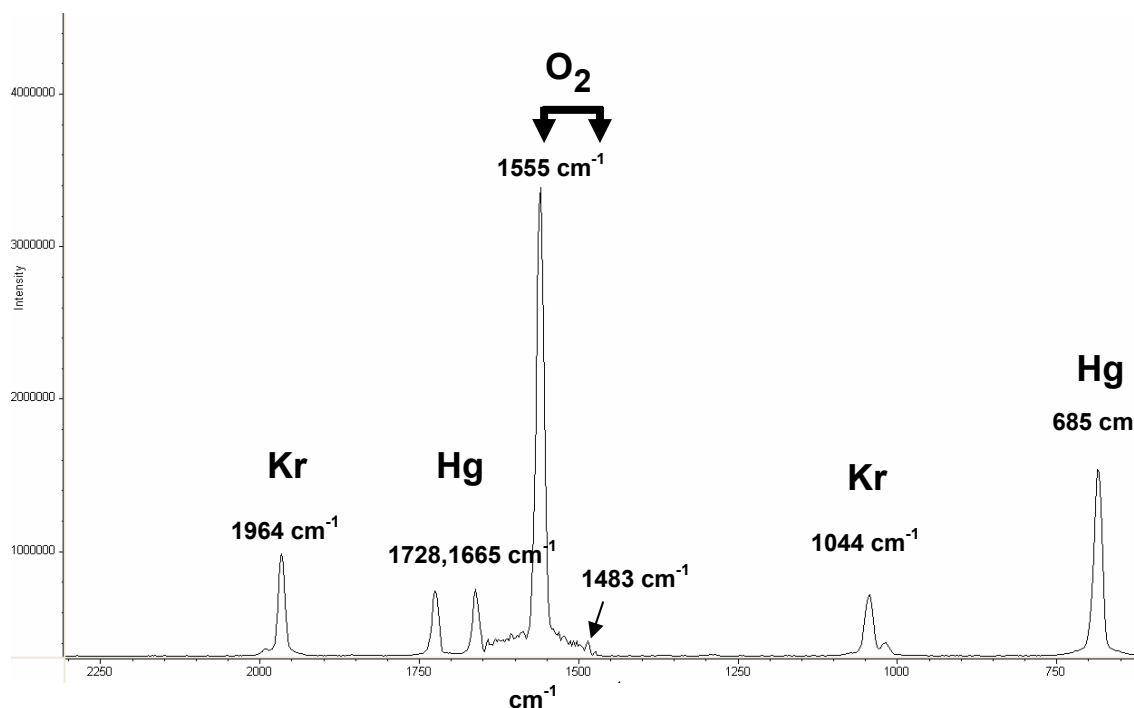
Figure A-1. Calibration Lines For Raman Spectra

These seven data points were used to convert the OMA pixels to corresponding wavenumbers for all Raman data in this report. In Figure A-2 the direct IR emission from singlet delta oxygen at 1.27 microns during the microwave discharge of an O_2/He mixture at 8.6 torr total pressure is shown for a one second data integration. The time-correlated Raman spectrum from this same discharged mixture is shown in Figure A-3 for a 10 second data integration. An arrow in Figure A-3 points to a feature that is nearly buried in the noise at 1483 cm^{-1} and it corresponds to $^1\Delta O_2$. Forty four consecutive 10 second Raman traces were averaged in Figure A-4 to highlight the weak $^1\Delta O_2$ feature which appears as a shoulder on the ground state oxygen signature.   The ground state oxygen spectrum obtained with the discharge off was software subtracted from
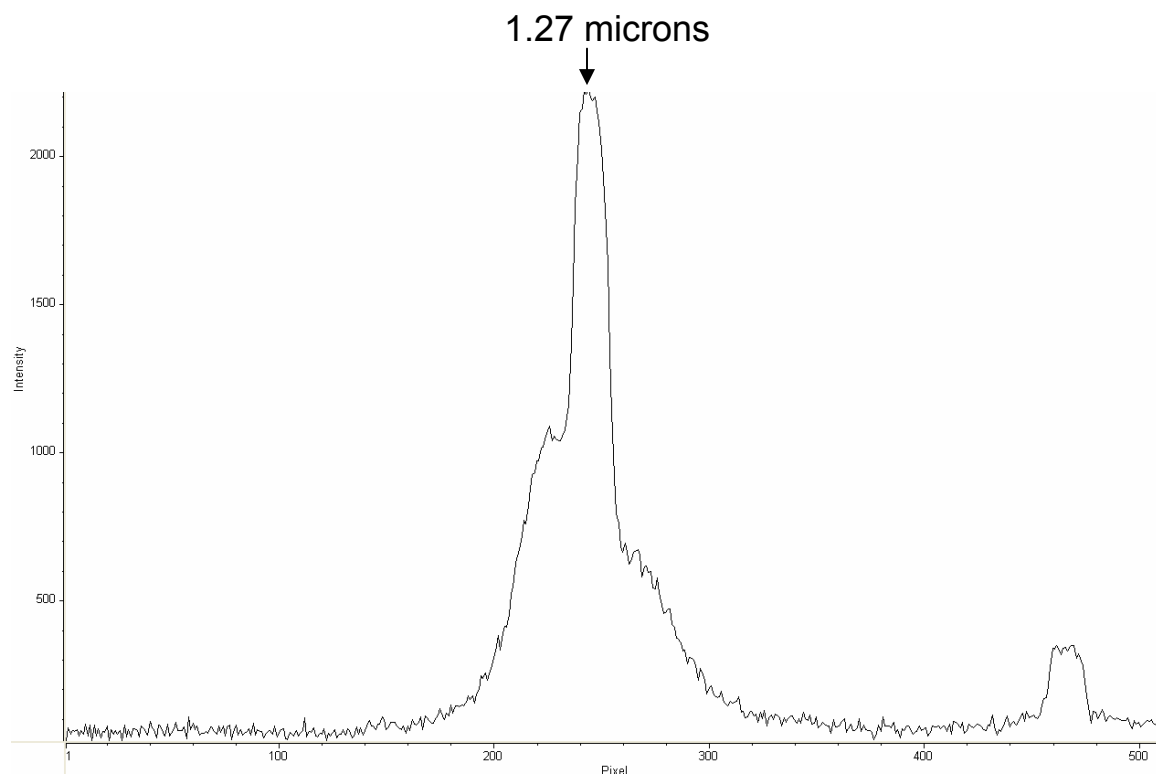
1.27 microns

Figure A-2, IR Emission from $^1\Delta O_2$ at 1.27 Microns

1483 cm^{-1}

cm^{-1}
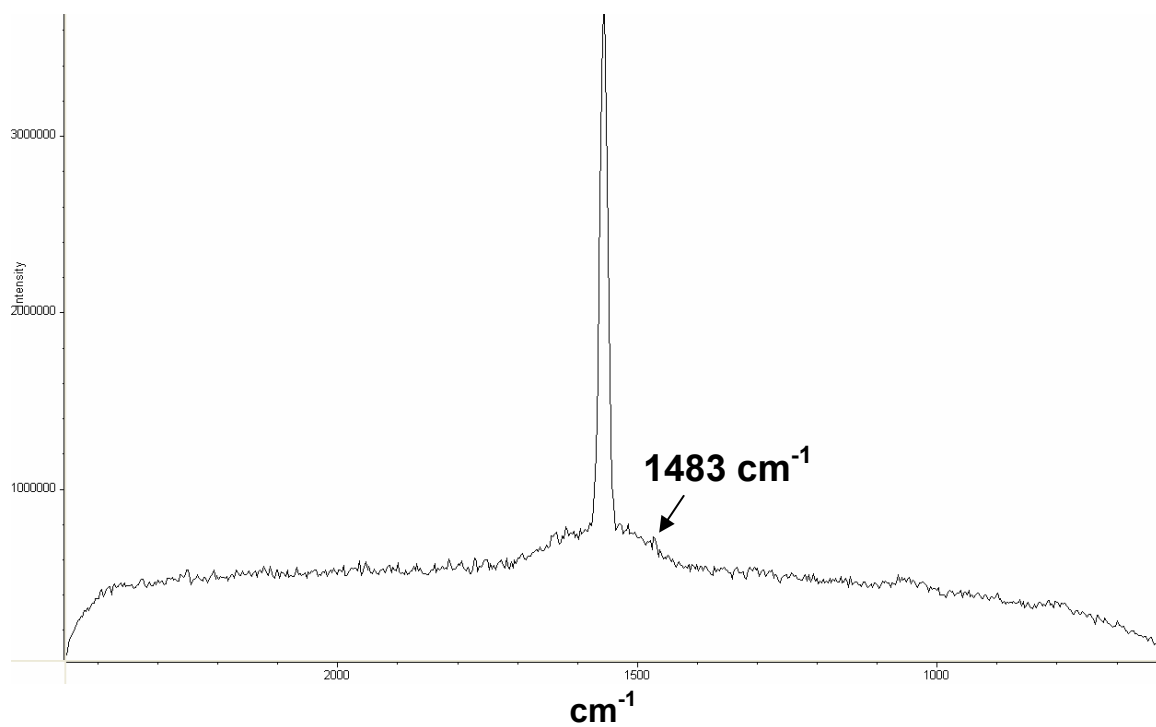
Figure A-3. Raman Spectrum from He/O$_2$ Microwave Discharge

Figure A-4 to produce Figure A-5 where the $^1\Delta O_2$ shoulder at 1483 cm^{-1} in Figures A-3 and A-4 is clearly visible.

The area of this peak corresponds to a $^1\Delta O_2$ pressure of 107 millitorr (3.5×10^{15} molecules/cc at 25C) and the area of the ground state oxygen peak represents 3.7 torr. These absolute concentrations were obtained from signal intensities on known oxygen pressures and known relative Raman cross sections for ground and $^1\Delta$ state oxygen. This 3% yield of $^1\Delta O_2$ in a He/O$_2$ discharge with no special efforts to enhance $^1\Delta O_2$ production is typical of published results. The 3.5×10^{15} molecules/cc of $^1\Delta O_2$ from Figure A-5 corresponds to the integrated IR emission signal strength in Figure A-2 of 96,074 counts/sec. The relationship between the concentration of singlet delta oxygen, $[^1\Delta O_2]$, and the IR emission signal is expressed in Equation (A1):

$$[^1\Delta O_2] \; x \; \varphi_e \; x \; 1/t \; x \; \varepsilon \; = \; \text{IR counts/sec} \tag{A1}$$

The value of ε is the product of the cell volume, the emission collection probability, and the detection probability; t is the time over which the emission occurs, and φ_e is the quantum yield (or probability) of emission. Equation (A1) highlights the fact that the Raman measurement of a $^1\Delta O_2$ concentration must be corrected for the $^1\Delta O_2$ loss due to nonradiative quenching by the φ_e term to obtain the radiative contribution on the RHS of the equation. The term φ_e is τ/τ_o which is the ratio of the $^1\Delta O_2$ lifetime at the total experimental pressure to the natural radiative lifetime (2700 sec). The microwave discharge consisted of a mixture of 3.7 torr (1.2×10^{17} molecules/cc) O_2 , 3.5×10^{15} molecules/cc of $^1\Delta O_2$ (O_2 *), and 4.9 torr (1.6×10^{17} molecules/cc) He, the value of τ is given by Equation (A2):

$$1/\tau = k_Q = k_{O2}[O_2] + k_{He}[H_e] + k_{O2}*[O_2*] + 1/\tau_o \tag{A2}$$
and * denotes the $^1\Delta$ state of oxygen

The values of the $^1\Delta O_2$ bimolecular quenching rate constants, k_i, for oxygen (1.5×10^{-18} cc/molecule-sec), singlet delta oxygen (2×10^{-17} cc/molecule-sec), and He (8.0×10^{-21} cc/molecule-sec) are published values. Equation (A2) gives a numerical value for τ of 4.0 seconds. The quantum yield of $^1\Delta O_2$ emission, φ_e , is τ/τ_o or $4.0/2700 = 1.5 \times 10^{-3}$. The term t in Equation

(A1) refers to the time over which the radiative channel is operative or the observation time, whichever is shorter. In our flowing microwave discharge experiment the IR emission signal persists for 2.1 seconds after the microwave power is shut off. In that time 41% of the emission from the $^1\Delta O_2$ with a 4.0 second lifetime would be observed. (The vacuum pump evacuates the cell faster than the excited states relax via emission.) Substituting for all the terms in Equation (A1):

$$(3.5\times10^{15} \text{ molecules/cc}) \,(1.5\times10^{-3}) \,(0.41/\,2.1\text{sec}) \ \ \varepsilon \ = \ 96{,}074 \text{ counts/sec} \qquad\qquad \text{(A3)}$$

This gives a value for the lumped experimental factor ε of 1.0×10^{-7} cc-counts/molecule. (Following a joint experiment at EAFB, Boeing calculated and reported a very close estimate of 1.8×10^{-7} for ε based only upon the experimental optical geometry, the estimated cell volume, and vendor specs for the IR OMA detector.)
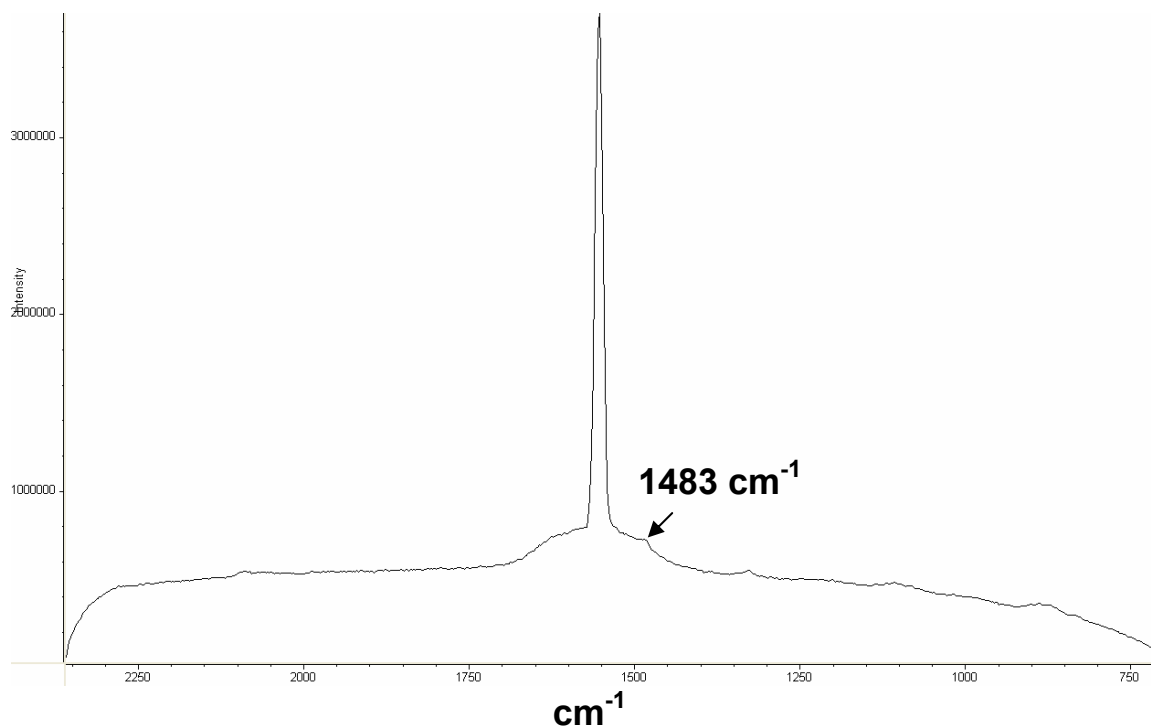
Figure A-4. Averaged Raman Spectrum from He/O$_2$ Microwave Discharge
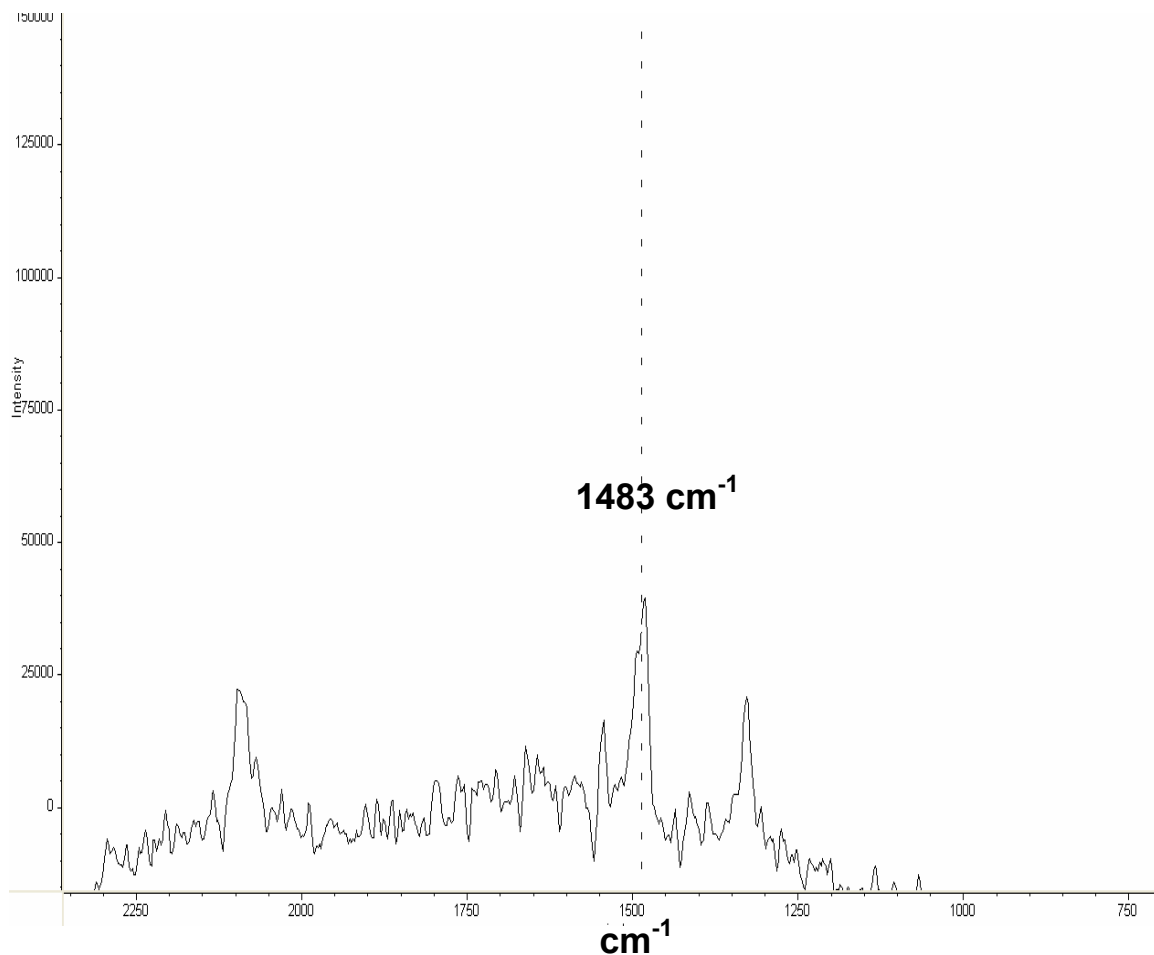
Figure A-5. Raman Spectrum Of O₂/He Discharge with Ground State Oxygen Subtracted

The experimentally corroborated value for ε, 1.0×10^{-7} cc-counts/molecule, permits the approximate calculation of the $^1\Delta O_2$ concentration from a measured IR emission signal in a static sodium peroxide-HCl experiment.

$$[^1\Delta O_2] \ x \ \varphi_e \ x \ \varepsilon \ = \ \text{Total IR counts} \tag{A4}$$

$$[^1\Delta O_2] = \ (\text{Total IR counts}) \ /(1.0 \times 10^{-7} \ \varphi_e) \tag{A5}$$

It is also noteworthy that this agreement between ε values validates the AFRL interpretation and application of the Stern-Volmer equation and the principles of pressure dependent emission quenching.

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APPENDIX B: U.S Patent 6,623,718 B1

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(12) **United States Patent** (10) **Patent No.:** **US 6,623,718 B1**

Christe et al. (45) **Date of Patent:** **Sep. 23, 2003**

(54) **PROCESS FOR THE CHEMICAL GENERATION OF SINGLET DELTA OXYGEN**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 95 days.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,461,756 A	*	7/1984	Rockenfeller	....	423/579
5,378,449 A	*	1/1995	Dinges	....	423/579
5,624,654 A	*	4/1997	Clendening et al.	....	423/579
6,165,424 A	*	12/2000	Clendening et al.	....	422/235

* cited by examiner

Primary Examiner—Stanley S. Silverman
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(74) Attorney, Agent, or Firm—Walter Unterberg

(57) **ABSTRACT**

This method generates the first electronically excited state of oxygen (singlet delta) at ambient temperature by a gas-solid chemical reaction involving a solid alkali metal peroxide or a solid alkaline earth peroxide and a non-radioactive-hydrogen-isotope halide gas. Singlet delta oxygen was produced from solid lithium peroxide, sodium peroxide or barium peroxide by reaction with gaseous hydrogen chloride, hydrogen bromide, deuterium chloride, or deuterium bromide. The method can be practiced in a static or a flow system, and the reaction may take place in a chemical oxygen-iodine laser. The described process avoids unstable precursors, such as basic hydrogen peroxide, and liquid phase quenching. The method is safe, compact, solvent-free, mechanically simple, requires no external energy source, and permits the generation of large quantities of singlet delta oxygen. Furthermore, since no liquid phase separations are required the process is ideally suited for zero gravitational force conditions.

25 Claims, No Drawings

# PROCESS FOR THE CHEMICAL GENERATION OF SINGLET DEL OXYGEN

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an improved method of chemically generating singlet delta oxygen. It particularly relates to a gas-solid reaction involving a hydrogen halide gas or deuterium halide gas and a solid alkali metal peroxide or solid alkaline earth peroxide.

2. Related Art

The singlet delta ($^1\Delta g$) state of oxygen, its first electronically excited state, lies 7874 cm^{-1} (1.27 microns) above the triplet sigma ground state. Singlet delta oxygen was first discovered in 1924 and has found wide application as an oxidizer[1,2] and energy transfer agent[3,4]. Its role in biological processes[5] (cell/tissue destruction, aging and cancer inducing processes), synthetic organic chemistry[1,2], airborne environmental and waste treatment chemistry, and the chemical oxygen iodine laser (COIL)[3,4,6] is well documented. A variety of methods have been used to produce singlet delta oxygen either from oxygen containing reagents or directly from oxygen. The documented reaction[6] used to produce singlet delta oxygen for the COIL is exemplified in equation (1):

$$2MOH + H_2O_{2(aq)} + Cl_2 \rightarrow O_2(^1\Delta g) + 2MCl + 2H_2O \qquad (1)$$
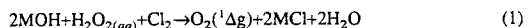
M in equation (1) is an alkali metal or mixture[7] thereof The aqueous environment represented by equation (1) is known to deactivate the singlet delta oxygen by collisional quenching and methods for very rapid and efficient oxygen extraction are required for COIL applications[8]. The hazards associated with concentrated basic hydrogen peroxide are also a disadvantage common to all coil embodiments based upon equation (1) and these hazards necessitate considerations for reaction zone cooling and maximum peroxide utilization and regeneration[7,9-12].

A variety of chemical sources of singlet delta oxygen has been reported[13]. These are typically solution based reactions that include analogs of equation (1). The reaction between gaseous ozone and certain organic substrates in the gas phase leads to singlet delta oxygen formation[14]. However, this approach is of no practical value in view of the hazards and difficulties associated with producing and handling ozone. Preparative oxidation chemistry methods which utilize singlet delta oxygen are generally limited to substrates soluble in water or in a suitably modified solvent system.

Direct photophysical techniques[15] that generate singlet delta oxygen from ground state oxygen require high powered light sources and inconvenient, dangerous pressures (100 atm) in purely gaseous or gas-liquid systems. Microwave or rf discharge of oxygen-gas mixtures are reliable techniques[16,17] for producing singlet delta oxygen at low total pressures of ca. 5 torr. A number of possibly undesirable species, including oxygen atoms, are also formed in the discharge process.

References Cited

1. A. A. Frimer and L. M. Stephenson. The singlet oxygen ene reaction, in Singlet O$_2$, Vol. 2, A. A. Frimer, ed., CRC Press, Boca Raton, Fla., 1984. Ch. 3.
2. R. F. Gould, ed., Oxidation of organic compounds, Vol. 3, Ozone chemistry, photo and singlet oxygen and biochemi-

cal oxidations, Advances in Chemistry, Vol. 77 (American Chemical Society, Washington, D.C., 1969.
3. W. E. McDermott, N. R. Pchelkin, D. J. Benard, and R. R. Bousek, An electronic transition chemical laser., Appl. Phys. Lett. 32, 469 (1978).
4. D. J. Benard, W. E. McDermott, N. R. Pchelkin, and R. R. Bousek, Efficient operation of a 100-W transverse-flow oxygen-iodine laser., Appl. Phys. Lett. 34, 40 (1979).
5. A. U. Khan, The discovery of the chemical evolution of singlet oxygen., Int. J. of Quantum Chem. 39, 251 (1991).
6. R. I. Wagner, Singlet delta oxygen generator and process., U.S. Pat. No. 4,310,502, Jan. 12, 1982.
7. C. W. Clendening, W. D. English, M. H. Mach, and T. D. Dreiling, Gas generating system for chemical lasers., U.S. Pat. No. 5,624,654, Apr. 29, 1997.
8. R. A. Dickerson, Singlet delta oxygen generator., U.S. Pat. No. 5,516,502, May 14, 1996.
9. J. D. Rockenfeller, Singlet delta oxygen generator., U.S. Pat. No. 4,461,756, Jul. 24, 1984.
10. W. L. Dinges, Formation of basic hydrogen peroxide., U.S. Pat. No. 5,378,449, Jan. 3, 1995.
11. W. E. McDermott, Singlet delta oxygen generator and process., U.S. Pat. No. 5,417,928, May 23, 1995.
12. D. G. Beshore and D. Stelman, Salt free lithium hydroxide base for chemical oxygen iodine laser., European Patent EP 0 819 647 A2, Jan. 21, 1998.
13. R. W. Murray, Chemical sources of singlet oxygen, in Singlet Oxygen H. H. Wasserman and R. W. Murray, ed., Academic Press, New York, N.Y., 1979, Ch. 3.
14. W. C. Eisenberg, K. Taylor, and R. W. Murray, Gas-phase generation of singlet oxygen by reaction of ozone with organic substances., J. Am. Chem. Soc. 107 8299 (1985).
15. W. C. Eisenberg, Atmospheric gas phase generation of singlet delta oxygen., in Advances in Oxygenated Processes, Vol. 3, pages 71–113, A. L. Baumstark, ed., JAI Press Inc., 1991.
16. S. M. Anderson, J. Morton, K. Mauersberger, Y. L. Yung, and W. B. DeMore, A study of atom exchange between O$_2$($^1\Delta$) and ozone, Chem. Phys. Lett. 189 581 (1992).
17. J. Schmiedberger and H. Fujii, Radio-frequency plasma jet generator of singlet delta oxygen with high yield, Appl. Phys. Lett. 78, 2649 (2001).

OBJECTS OF THE INVENTION

It is, therefore, an object of this invention to provide a technique that produces singlet delta oxygen in high yield from readily available starting materials in a minimally quenching environment without the need for external electrical, optical, or thermal energy.

Another object is to provide a safe method that avoids the use of dangerous, explosive chemicals such as basic hydrogen peroxide.

Yet another object is to provide a process that avoids the need for separating gases from a liquid phase thus rendering it suitable for zero gravity conditions.

A further object is to provide a lightweight, readily scalable, and mechanically simple method that avoids the use of heavy complex machinery, such as vortex mixers, centrifuges, and vacuum pumps to extract excited state oxygen from solution.

SUMMARY OF THE INVENTION

To implement the objects stated above, the method of the present invention was devised in which singlet delta oxygen is generated by a chemical reaction at ambient temperature

of a solid peroxide with a hydrogen halide gas or a deuterium halide gas, without using external energy sources.

Singlet delta oxygen was produced from an alkali metal peroxide (such as lithium peroxide or sodium peroxide) or an alkaline earth peroxide (such as barium peroxide) in a reaction with a non-radioactive-hydrogen-isotope halide gas (such as hydrogen chloride, hydrogen bromide, deuterium chloride, or deuterium bromide). A static gas fill system was used and the results were observed by emission spectroscopy. Comparable results can be obtained in a flow system, and further, the reaction may take place in a chemical oxygen-iodine laser.

Accordingly, the present invention provides a safe, compact, lightweight, readily scalable, and highly efficient method for producing singlet delta oxygen from commercially available starting materials by directly reacting a solid peroxide with a non-radioactive-hydrogen-isotope halide gas. It avoids the use of unstable starting materials, such as basic hydrogen peroxide that can explode, and liquid phase quenching that can rapidly destroy most of the desired singlet delta oxygen. Furthermore, it avoids the need for a gas-liquid phase separation, thus making it ideal for space-based applications under zero gravity conditions.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is the chemical generation of singlet delta oxygen by a gas-solid reaction at ambient temperature without external energy sources. A dry, solid alkali metal peroxide or solid alkaline earth peroxide is reacted with a dry hydrogen halide gas or a dry deuterium halide gas to form singlet delta oxygen. Alkali metal peroxides include lithium peroxide, Li_2O_2, and sodium peroxide, Na_2O_2; alkaline earth peroxides include barium peroxide, BaO_2. Non-radioactive-hydrogen-isotope halide gases include hydrogen chloride, HCl, hydrogen bromide, HBr, deuterium chloride, DCl, and. deuterium bromide, DBr.

All of these materials can be handled safely and are readily available commercially. Furthermore, the reactions of this invention do not require any external energy sources, such as photolysis, discharge, or heat. The desired singlet delta oxygen gas can be generated either in a static or a flow system. In a static system, a suitable peroxide is pressurized with a desired amount of the corresponding hydrogen halide gas or deuterium halide gas, resulting in continuous singlet delta oxygen evolution. In a flow system, a controlled stream of hydrogen halide gas or deuterium halide gas is passed either through a fixed bed of solid peroxide or introduced into a bed of fluidized peroxide, with the latter approach providing increased mixing, conversions, and space utilization. The resulting major products are solid metal halides, water vapor, and singlet delta oxygen gas, $O_2(^1\Delta g)$, as shown in equation (2) for the reaction of Na_2O_2 and HCl:

$$2Na_2O_2 + 4HCl \rightarrow 4NaCl + 2H_2O + O_2(^1\Delta g) \qquad (2)$$
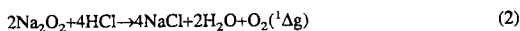
The preferred peroxides of our invention are alkali metal peroxides and, particularly, lithium peroxide, Li_2O_2, and sodium peroxide, Na_2O_2. However, other peroxides, such as alkaline earth peroxides, particularly barium peroxide, BaO_2, can also be used in place of the alkali metal peroxides. Further, the reaction may take place in a chemical oxygen-iodine laser.

Among the non-radioactive-hydrogen-isotope halides of our invention, HCl and HBr are preferred, with HBr producing the most intense singlet delta oxygen signals, followed by HCl. Since deuterated compounds quench singlet oxygen to a lesser extent than the corresponding hydrogen analogues, the use of DCl or DBr in place of HCl or HBr, respectively, is of particular interest for this invention.

Factors, such as solid surface area and dryness of the starting peroxide may affect these results.

EXPERIMENTAL PROCEDURE

The formation of singlet delta oxygen in our reactions was monitored by the observation of direct emission from the normally forbidden transition of singlet delta to ground state triplet sigma O_2 at 1.27 microns using a liquid nitrogen cooled InGaAs optical multichannel analyzer (OMA) after dispersion with an 0.3 meter spectrograph. The singlet delta oxygen emission signal obtained was identical in wavelength position and contour to that obtained from a microwave discharge of a helium-oxygen mixture at 4 torr and from a small sparger that reacted chlorine gas with basic hydrogen peroxide (BHP) according to equation (1). The sparger contained 100 cc of a mixture that was 7.5 M in H_2O_2 and 1.1 M in NaOH. The BHP was kept at −10 C and ca. 160 sccm of Cl_2 was bubbled through the liquid. A vacuum pump preceded by a liquid-nitrogen cooled trap extracted oxygen from the sparger at 6 torr total pressure. These two techniques are reliable standards for producing quantities of singlet delta oxygen that are readily observable by emission spectroscopy.

The following non-limitative examples illustrate the invention:

EXAMPLE 1

Hydrogen Chloride-Sodium Peroxide, HCl—Na_2O_2

A 7 inch path length cell made of 0.5 inch o.d. Pyrex glass with separate, side-mounted 0.25 inch diameter gas inlet and evacuation ports was used. This cell was terminated on one end with an O-ring joint that mated to a near infrared transmitting window with a 0.38 inch diameter clear aperture. The unthermostated cell contained 400 milligrams of sodium peroxide at room temperature and was slowly pressurized with hydrogen chloride gas up to 600 torr. The reaction cell was positioned with the window a few millimeters. from the entrance slit of an 0.3 meter spectrograph with an InGaAs (−113 C) OMA mounted in the exit plane. The direct emission from O_2 singlet delta was readily observed in the 1.27 micron region both during the gas fill and after gas addition was stopped. The reaction was not violent but the cell pressure fell with time and the emission signal increased with added HCl pressure. Repeatedly pumping out and recharging the cell with HCl afforded approximately two hours of singlet delta oxygen emission from the same 400 milligram sodium peroxide sample. Signal collection times as short as one second were adequate for capturing clear $^1\Delta O_2$ emission spectra. The reaction product was a colorless solid.

EXAMPLE 2

Hydrogen Bromide-Sodium Peroxide, HBr—Na_2O_2

A 400 mg sample of Na_2O_2 was added to the unthermostated cell described in Example 1 and was slowly pressurized at room temperature with hydrogen bromide gas to 230 torr over a 9 minutes period. The reaction cell was positioned with the window a few millimeters from the entrance slit of an 0.3 meter spectrograph with an InGaAs (−113 C) OMA mounted in the exit plane. The direct emission from O_2 singlet delta was readily observed in the 1.27 micron region. Singlet delta oxygen emission signals were significantly stronger in this case than with HCl as the gaseous reactant and detector saturation resulted. The HBr/Na_2O_2 reaction was not violent. The cell was pumped out and recharged with HBr to 150 torr over an 8 minutes period and strong emission was observed at reduced slit widths and

5

6

integration times. The HBr pressure was further increased to 270 torr over eight minutes and the emission fell to 25% of the original signal strength at 150 torr after 10 minutes. Appreciable $^1\Delta O_2$ emission was recorded for an additional sixteen minutes. The reaction product was a colorless solid.

EXAMPLE 3

Hydrogen Chloride-Barium Peroxide, HCl—BaO$_2$

A 700 mg sample of BaO$_2$ was added to the unthermostated cell described in Example 1 and was slowly pressurized at room temperature with hydrogen chloride gas to 420 torr over a 6 minutes period. The reaction cell was positioned with the window a few millimeters from the entrance slit of an 0.3 meter spectrograph with an InGaAs (–113 C) OMA mounted in the exit plane. The direct emission from singlet delta O$_2$ was not observed until 4 minutes later in the 1.27 micron region. Singlet delta oxygen emission signals persisted for another 12 minutes. The HCl/BaO$_2$ reaction was not violent. The cell was pumped out and recharged with HCl to 440 torr over a two minute period and no emission was observed during an additional 14 minutes. The solid reaction product was colorless and it resembled unreacted BaO$_2$.

EXAMPLE 4

Deuterium Chloride-Sodium Peroxide, DCl— Na$_2$O$_2$

A 400 mg sample of Na$_2$O$_2$ was added to the unthermostated cell described in Example 1 and was slowly pressurized at room temperature with deuterium chloride gas to 280 torr over a 15 minutes period. The singlet delta oxygen emission signal was detected after 6 minutes and continued to grow until the observation was terminated at 20 minutes. The gaseous contents of the cell were then condensed in a liquid nitrogen cold trap and DCl was added until the pressure reached 440 torr at 20 minutes. The maximum oxygen emission was obtained between 6 and 8 minutes at a total cell pressure of 100 to 200 torr. The gaseous contents of the cell were condensed at –77K and further addition of DCl resulted in larger oxygen emission signals at 1.27 microns. The cell was evacuated for 15 hours and a strong singlet delta oxygen emission signal was obtained when 120 torr of DCl was added. A colorless solid was recovered from the cell.

EXAMPLE 5

Deuterium Bromide-Sodium Peroxide, DBr— Na$_2$O$_2$

A 400 mg sample of sodium peroxide was added to the unthermostated cell described in Example 1 and was slowly pressurized to 230 torr with deuterium bromide over 6 minutes. Singlet delta oxygen emission was observed after 2 minutes. Condensing the gaseous contents of the cell into a liquid-nitrogen cooled trap and recharging the cell with fresh DBr yielded oxygen emission that grew over a 20 minutes observation period. A yellow solid was recovered from the cell.

EXAMPLES 6 and 7

Hydrogen Chloride-Lithium Peroxide, HCl—Li$_2$O$_2$, and Hydrogen Bromide-Lithium Peroxide, HBr— Li$_2$O$_2$

When the Na$_2$O$_2$ in examples 1 and 2 was replaced by Li$_2$O$_2$, comparable yields of singlet oxygen were obtained under the same reaction conditions.

As will be apparent to those skilled in the art, numerous modifications and variations of the present invention are possible in light of the above teaching. For example, the above examples have used a static gas fill system. However, for a continuous singlet oxygen generation process, a flow system obviously is the preferred choice. It is to be understood, therefore, that the invention may be practiced other than as specifically described herein within the scope of the appended claims.

What is claimed is:

1. A method for generating singlet delta oxygen at ambient temperature and without external energy sources, the method comprising a chemical reaction between a solid peroxide and a non-radioactive-hydrogen-isotope halide gas.

2. The method of claim 1 further comprising the use of a static gas fill system.

3. The method of claim 1 further comprising the use of a gas flow system.

4. The method of claim 1 further comprising its use in a chemical oxygen-iodine laser.

5. The method of claim 1 wherein said solid peroxide is an alkali metal peroxide.

6. The method of claim 1 wherein said solid peroxide is an alkaline earth peroxide.

7. The method of claim 1 wherein said non-radioactive-hydrogen-isotope halide gas is hydrogen chloride.

8. The method of claim 1 wherein said non-radioactive-hydrogen-isotope halide gas is hydrogen bromide.

9. The method of claim 1 wherein said non-radioactive-hydrogen-isotope halide gas is deuterium chloride.

10. The method of claim 1 wherein said non-radioactive-hydrogen-isotope halide gas is deuterium bromide.

11. The method of claim 5 wherein said solid alkali metal peroxide is sodium peroxide.

12. The method of claim 5 wherein said solid alkali metal peroxide is lithium peroxide.

13. The method of claim 6 wherein said alkaline earth peroxide is barium peroxide.

14. The method of claim 7 wherein said solid peroxide is lithium peroxide.

15. The method of claim 7 wherein said solid peroxide is sodium peroxide.

16. The method of claim 7 wherein said solid peroxide is barium peroxide.

17. The method of claim 8 wherein said solid peroxide is lithium peroxide.

18. The method of claim 8 wherein said solid peroxide is sodium peroxide.

19. The method of claim 8 wherein said solid peroxide is barium peroxide.

20. The method of claim 9 wherein said solid peroxide is lithium peroxide.

21. The method of claim 9 wherein said solid peroxide is sodium peroxide.

22. The method of claim 9 wherein said solid peroxide is barium peroxide.

23. The method of claim 10 wherein said solid peroxide is lithium peroxide.

24. The method of claim 10 wherein said solid peroxide is sodium peroxide.

25. The method of claim 10 wherein said solid peroxide is barium peroxide.

* * * * *

APPENDIX C: AFRL Technology Horizons Article

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PR A Gas-Solid Singlet Delta Oxygen Generator for the Chemical Oxygen-Iodine Laser

Scientists discover new chemistry for producing a key component of a chemically pumped laser.

AFRL's Propulsion Directorate, Space and Missile Propulsion Division, Propellants Branch, Edwards AFB CA

In 1978, Dr. William McDermott and coworkers invented the chemical oxygen-iodine laser (COIL), the predecessor of major programs in today's Directed Energy Directorate.[1] The technique involved passing chlorine gas through aqueous basic hydrogen peroxide to produce electronically excited singlet delta oxygen. The direct relaxation of singlet delta oxygen to the ground state by the emission of radiation is quantum mechanically forbidden, but an

experimentalist can observe a weak emission. Therefore, the device must transfer the energy available from the chlorine-basic hydrogen peroxide chemical reaction from the excited oxygen to an efficient light emitter. This transfer partner should have an energy level close to the 1.27 μm excited oxygen state to facilitate the energy transfer.[2] The iodine atom, which has a 1.3 μm excited state, is well suited for this purpose. However, the efficiency of the energy transfer to iodine atoms is reduced due to collisions between excited state oxygen and other species within the liquid reaction medium. The main collision partners are water, hydrogen peroxide, and oxygen. This nonradiative relaxation results in the creation of undesired heat rather than the desired light emission. Several patented developments address the need to rapidly extract the excited oxygen from its quenching aqueous environment and efficiently mix it with iodine for subsequent lasing at 1.3 μm.[3] These enhancements add further complexity and weight to a reaction chemistry that also involves the preparation and handling of unstable basic hydrogen peroxide.

To circumvent the problems associated with the aqueous COIL chemistry, the Directed Energy Directorate developed the all gas-phase iodine laser (AGIL).[4] The AGIL laser produces excited nitrogen chloride from chlorine atoms and gaseous hydrogen azide. The excited nitrogen chloride transfers energy to iodine atoms to produce a 1.3 μm laser wavelength, which is well propagated through the atmosphere. However, the explosion hazard of hydrogen azide's chemistry in the AGIL compromises the advantage of eliminating the aqueous basic hydrogen peroxide chemistry in the COIL.

In an effort to improve the safety and reduce the complexity of the COIL and AGIL concepts, the Defense Advanced Research Projects Agency funded an idea from chemists in the Propulsion Directorate at Edwards Air Force Base, California, to investigate alternative means of preparing singlet delta oxygen from safe starting materials while avoiding liquid-phase quenching problems. The chemists investigated solid-solid, solid-pyrolysis, and gas-solid reactions. A breakthrough emerged when they produced singlet delta oxygen with solid alkali metal/alkaline earth peroxides and gaseous hydrogen/deuterium halides. The chemists verified production of singlet delta oxygen by observing its emission at 1.27 μm and comparing the emission wavelength and band contour with well-known singlet delta oxygen sources such as an oxygen-helium microwave discharge and a basic hydrogen peroxide/clorine sparger. The chemists performed gas-solid reactions in a static system by admitting hydrogen/deuterium halide gas (up to 700 torr) to an evacuated cell containing the solid peroxide at room temperature. The nonhazardous, commercially available reagents react nonviolently, and the products are oxygen, water, and benign alkali metal or alkaline earth-halide salts. Further development of this concept could provide an improved singlet delta oxygen generator that utilizes the COIL technology for iodine atom production, oxygen-iodine atom mixing, and 1.3 μm laser light extraction. An improved singlet delta oxygen generator, based upon the newly discovered gas-solid chemistry, would offer significant operational improvements in COIL technology while preserving COIL's inherent advantage of single line emission at 1.3 μm. Since the need for gas-liquid separation is precluded, these gas-solid reactions are also well suited for both reduced and high-gravity environments. Researchers believe that the Airborne and Space-Based Laser programs would both benefit from the combined advantages of this innovative excited-state oxygen generator and existing technology.

Dr. Angelo Alfano and Dr. Karl Christe (ERC, Inc.), and Dr. Robert Corley of the Air Force Research Laboratory's **Propulsion Directorate** *wrote this article. For more information contact TECH CONNECT at (800) 203-6451 or place a request at http://www.afrl.af.mil/techconn/index.htm. Reference document PR-02-04.*

References
[1] Benard, D. J., Bousek, R. R., McDermott, W. C., and Pchelkin, N. R. *Appl. Phys. Lett.*, 32, pp. 469, 1978.
[2] Calvert, J. G. and Pitts, J. N. *Photochemistry.* New York: John Wiley & Sons, 1966.
[3] (a) Wagner, R. I. US Patent 4,310,502 (1982).
(b) MacKnight, A. K. and Stancliffe, A. C. US Patent 4,342,116 (1982).
(c) Rockenfeller, J. D. US Patent 4,461,756 (1984).
(d) McDermott, W. E. US Patent 5,516,502 (1995).
(e) Dickerson, R. A. US Patent 5,516,502 (1996).
[4] (a) Berman, M. R., Hager, G. D., Henshaw, T. L., Madden, T. J., and Manke II, G. C. "New Chemically Pumped Laser." *AFRL Technology Horizons®*, vol 2, no 1 (Mar 01), 20-21.
(b) Manke II, G. C. "A New All Gas-Phase Chemical Iodine Laser." *AFRL Technology Horizons®*, vol 3, no 1 (Mar 02), 21.
(c) Berman, M. R., Hager, G. D., Henshaw, T. L., Madden, T. J., and Manke II, G. C. *Chem. Phys. Lett.*, 325, pp. 537, 2000.

APPENDIX D: Angewandte Chemie International Edition Article

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Singlet Delta Oxygen Production from a Gas – Solid Reaction

$^1\Delta$-O_2 can now be made safely and efficiently from gas–solid reactions between alkali-metal peroxides and hydrogen halides [Eq. (1)]. This method avoids the liquid-phase quenching and instability problems associated with the hydrogen peroxide/chlorine system.

$$Na_2O_2 + 2\,HCl \longrightarrow H_2O + 2\,NaCl + 1/2\,O_2\ (^1\Delta_g) \tag{1}$$
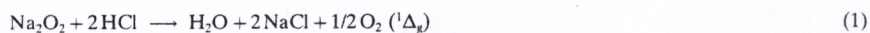
A. J. Alfano,
K. O. Christe* 3252–3254

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COMMUNICATIONS

Singlet Delta Oxygen Production from a Gas–Solid Reaction**

Angelo J. Alfano and Karl O. Christe*

Dedicated to Dr. Robert Corley

The long and interesting history of singlet delta ($^1\Delta_g$) oxygen, including its discovery, study, understanding, and applications, has been described in several publications.[1–4] The singlet delta state is the lowest lying excited electronic state of oxygen and it differs from the triplet ground state, $^3\Sigma_g^-$, in spin multiplicity. The generation of $^1\Delta_g$ O_2 from ground state $^3\Sigma_g^-$ O_2, using direct electronic excitation, is spin forbidden and inherently inefficient.[5] Therefore, either complex chemical reactions that produce intermediates capable of spontaneously eliminating electronically excited O_2, or compounds that can decompose directly to produce excited state oxygen have been studied for $^1\Delta_g$ O_2 production. Typical examples include: hydrogen peroxide with aqueous hypochlorite,[6] basic hydrogen peroxide (BHP) with molecular halogens or phenols,[7] the superoxide anion with water,[4,8] ozone with organic substrates such as triaryl phosphates,[9] alkaline peroxo acids,[7,10] organic peroxides,[11] and transition-metal–oxygen complexes.[12] Although some of these reactions efficiently generate $^1\Delta_g$ O_2, they are all carried out in liquid-phase systems that cause quenching of the excited oxygen. The required rapid extraction of the gaseous singlet delta oxygen is very difficult. Furthermore, molecules capable of spontaneous elimination of electronically excited oxygen are thermodynamically unstable and, therefore, can present serious handling problems. Similar arguments may also apply to some of the precursors, such as the basic hydrogen peroxide in the BHP/Cl_2 system.[13] In view of the significance of an efficient and safe $^1\Delta_g$ O_2 generator for the chemical oxygen iodine laser (COIL)[14] and other chemical and biochemical applications,[1,4] the development of new methods that can overcome these problems is of great importance.

Herein, we describe chemical reactions that spontaneously and efficiently produce singlet delta oxygen from solid alkali metal or alkaline-earth metal peroxides and dry hydrogen-(deuterium) halide gases at room temperature. The reactions do not require external energy sources, such as heat, light, or

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electricity (discharge), and they avoid liquid-phase quenching and dangerous reagents.

The apparatus for generating and monitoring O_2 $^1\Delta_g$ from solid peroxides and gaseous hydrogen(deuterium) halides is depicted in Figure 1. The reaction/observation cell consisted
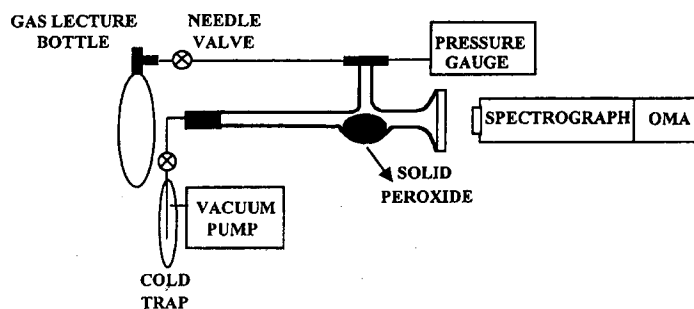

Figure 1. Apparatus for generating singlet delta oxygen and observing its emission.

of a 5 mm (i.d.) Pyrex glass tube that was attached to a 5 mm O-ring seal joint and a perpendicular sidearm. Opposite from the sidearm, the diameter of the tube was increased to provide a repository for the solid peroxide samples. A sodium chloride or an S-1 UV quartz window was clamped to the O-ring joint, and the whole assembly was placed 3 cm in front of an optical multichannel analyzer (OMA) spectrograph combination with the optical window facing the entrance slit. No collection optics were used.

In a typical experiment, 400 mg of a solid alkai metal or alkaline-earth metal peroxide was added to the cell within the dry nitrogen atmosphere of a glove box. The cell was installed into the test apparatus, evacuated, and dry hydrogen(deuterium) halide gas was added through the sidearm up to a maximum total pressure of 760 Torr. The OMA was kept at 160 K and an uninterrupted sequence of ten emission spectra (120 s collection time each) was recorded. Background subtraction was performed on all data. Several combinations of solid peroxide and gaseous hydrogen halide were tested: sodium peroxide/hydrogen(deuterium) chloride, sodium peroxide/hydrogen(deuterium) bromide, sodium peroxide/hydrogen iodide, barium peroxide/hydrogen chloride, barium peroxide/hydrogen bromide, and lithium peroxide/hydrogen chloride.

The O_2 $^1\Delta_g$ generation was monitored by the emission from its A→X ($^1\Delta_g$→$^3\Sigma_g^-$) spin-forbidden transition at 1.27 microns using a 0.3 m Czerny–Turner spectrograph with a 600 groove per mm grating blazed at 1 micron and a near-IR sensitive OMA. The emission was identical in wavelength and contour to those produced by either a microwave discharge of an oxygen–helium mixture[15] or a BHP–chlorine sparger[16] (see Figure 2 a and b, respectively).

All the above listed combinations of peroxide and gaseous hydrogen halide produced readily observable O_2 $^1\Delta_g$ emissions, except when hydrogen iodide was used. Figure 2 c shows the results obtained from sodium peroxide and 580 Torr of hydrogen chloride. The data represent an OMA exposure time of 120 s. Singlet delta oxygen emission from the Na_2O_2/HCl reaction was recorded for ten consecutive 120 s exposures
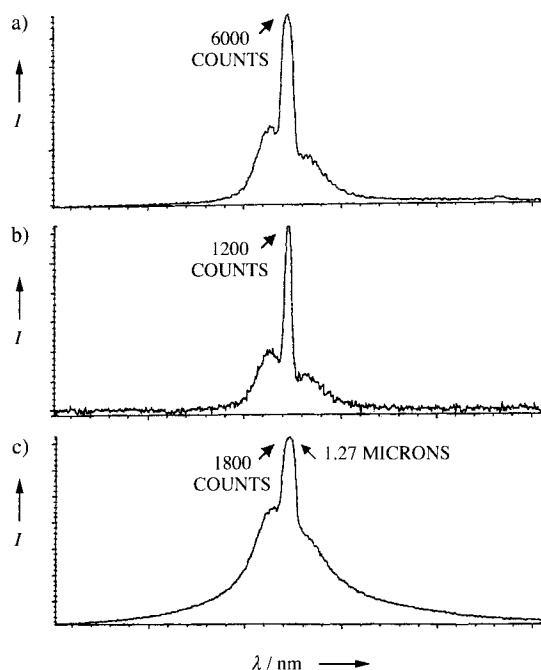
Figure 2. Emission spectra of singlet delta oxygen from a helium–oxygen microwave discharge (a; exposure time 1 s), a basic hydrogen peroxide/chlorine sparger (b; exposure time 1 s), and the Na_2O_2/HCl reaction system (c; exposure time 120 s).

under three different reaction pressure conditions. The pressure of the reaction cell was either maintained constant by repeated addition of HCl, allowed to fall as HCl was consumed, or increased by continuous addition of HCl. In the latter case, the emission increased logarithmically with pressure. Constant or decreasing cell pressures resulted in exponentially decreasing emission signals over a 20-minute period. At a constant cell pressure of 450 Torr, the observed decay of the excited state emission over a 20-minute observation period was four orders of magnitude slower than that predicted from the known quenching rates of HCl and water vapor.[18,19] These results demonstrate that the loss of emission due to quenching is largely offset by the continuous production of O_2 $^1\Delta_g$.

The stoichiometry of the sodium peroxide/HCl reaction was experimentally established by quantitatively analyzing the material balance on a vacuum line. The results are in excellent agreement with Equation (1).

$$Na_2O_2 + 2\,HCl \rightarrow H_2O + 2\,NaCl + 1/2\,O_2\ (^1\Delta_g) \tag{1}$$
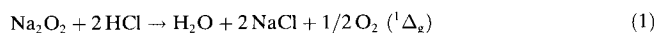
Equation (1) is also consistent with the condensation of some water vapor on the cell walls, the conversion of the yellow peroxide starting material to a white solid (NaCl), and a decrease in pressure as the emission data were recorded.

In Figure 2, the O_2 $^1\Delta_g$ emission signals from the microwave discharge, the BHP sparger, and the Na_2O_2/HCl system are compared. The discharge was operated with a flow rate of 1×10^{-5} mol of O_2 per second plus helium, and the sparger could produce a maximum of 1.2×10^{-4} mol of O_2 per second, assuming 100% chlorine utilization. A single sample of 5×10^{-3} mol of sodium peroxide was recharged ten times with 500

to 700 Torr of HCl and produced O_2 $^1\Delta_g$ emission for a total of 200 minutes. Although a quantitative comparison of these three O_2 $^1\Delta_g$ production methods is difficult due to the differences in exposure times, observation geometries, and signal durations, the gas–solid reaction must be considered a highly efficient source of excited oxygen based upon the duration and strength of the emission signal in nearly one atmosphere of a quenching gas.

An additional experiment was conducted with the sodium peroxide/hydrogen chloride pair to check for potential emission at 634 nm from the energy-pooling reaction [Eq. (2)]. At sufficiently high O_2 $^1\Delta_g$ concentrations, this

$$2\,O_2\ (^1\Delta_g) \rightarrow 2\,O_2\ (^3{\textstyle\sum}_g^-) + h\nu\ (634\,nm) \tag{2}$$
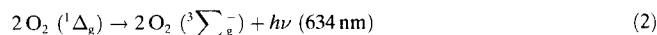
energy-pooling process is known to produce a visible red glow.[20] In our study, a separate OMA system sensitive in this region was used, but no evidence for this transition was found, possibly due to the dilution imparted by the high HCl pressure.

The other gas–solid reaction systems were tested in a larger cell that consisted of a 10 mm O-ring seal joint connected to a 7 inch length of 1/2 inch (o.d.) Pyrex tubing with 1/4 inch (o.d.) sidearms for gas inlet and evacuation. Larger amounts of sample were spread over a longer reaction zone, thus increasing the gas–solid contact time over that allowed by the cell of Figure 1. The listed reagent pairs were tested in a qualitative fashion. Typically, a one gram sample of solid peroxide was slowly pressurized with the hydrogen(deuterium) halide gas to 300 to 400 Torr. The gas was allowed to flow into the cell during the measurement so that the net pressure rose during the recording of the emission data. The emission from the sodium peroxide/hydrogen bromide system was especially strong and OMA saturation was experienced at exposure times of 120 s. The results from these tests are summarized in Table 1. The emission signal intensities varied

Table 1. Solid peroxides and gaseous hydrogen halides yielding singlet delta oxygen.

Peroxide	Hydrogen halide	Qualitative emission strength
Na_2O_2	HCl	strong
Na_2O_2	DCl	strong
Na_2O_2	HBr	very strong
Na_2O_2	DBr	very strong
BaO_2	HCl	medium
BaO_2	HBr	medium
Li_2O_2	HCl	strong

somewhat from experiment to experiment. This was partially due to small changes in the positioning of the sample cell after cleaning and reloading with fresh solid peroxide. The reactions with the deuterated halides are of special interest since deuterated compounds are significantly weaker quenchers than their hydrogen-containing counterparts.[21] Other simple systems were also tested. For example, potassium superoxide, KO_2, was allowed to react with hydrogen chloride, and a weak emission signal due to O_2 $^1\Delta_g$ was observed.

However, these systems are inferior to those involving the alkali metal and alkaline-earth metal peroxides.

In summary, the results of this study demonstrate the feasibility of efficiently generating singlet delta oxygen from gas–solid reactants without the problems associated with liquid-phase quenching. Furthermore, the required starting materials are commercially available, moderately priced, and safe to handle.

[1] *Singlet O₂* (Ed.: A. A. Frimer), CRC, Boca Raton, FL, **1985**.

[2] *Singlet Molecular Oxygen* (Ed.: A. P. Schaap), Dowden, Hutchinson & Ross, Stroudsburg, **1976**.

[3] *Singlet Oxygen* (Eds.: H. H. Wasserman, R. W. Murray), Academic Press, New York, **1979**.

[4] A. U. Khan, *Int. J. Quantum Chem.* **1991**, *39*, 251.

[5] W. C. Eisenberg, K. Taylor, J. Veltman, R. W. Murray, *J. Am. Chem. Soc.* **1982**, *104*, 1104.

[6] A. U. Khan, M. Kasha, *J. Chem. Phys.* **1963**, *39*, 2105.

[7] E. McKeown, W. A. Waters, *J. Chem. Soc. B* **1966**, 1040.

[8] A. U. Khan, *J. Am. Chem. Soc.* **1981**, *103*, 6516.

[9] Q. E. Thompson, *J. Am. Chem. Soc.* **1961**, *83*, 845.

[10] R. F. Boyer, C. G. Lindstrom, B. Darby, M. Hylarides, *Tetrahedron Lett.* **1975**, 4111.

[11] H. H. Wasserman, J. R. Scheffer, J. L. Cooper, *J. Am. Chem. Soc.* **1972**, *94*, 4991.

[12] J. W. Peters, P. J. Bekowies, A. M. Winer, J. N. Pitts, Jr., *J. Am. Chem. Soc.* **1975**, *97*, 3299.

[13] L. Bretherick, *Bretherick's Handbook of Reactive Chemical Hazards*, 4th ed., Butterworths, London, **1990**.

[14] F. Wani, M. Endo, T. Fujioka, *Appl. Phys. Lett.* **1999**, *75*, 3081.

[15] A 70 watt microwave discharge (2.45 GHz) of an oxygen–helium mixture at a total pressure of 5 Torr was used to record the $O_2\ ^1\Delta_g$ emission spectrum. At the typical flow conditions of the measurement 1×10^{-5} moles of oxygen were delivered per second. A glass wool plug was placed in the discharge tube to aid in the recombination of oxygen atoms. If the discharge, gas flow, and vacuum pumping were simultaneously stopped, the emission signal decayed within one second.

[16] The BHP–chlorine sparger contained 100 mL of an aqueous mixture that was 1.1 M in NaOH and 7.5 M in H_2O_2. It was prepared by slowly adding the NaOH to cold 85 % H_2O_2 over a 30-minute period while keeping the temperature of the mixture below 273 K. The sparger was immersed into a 258-K recirculating bath, and chlorine gas was introduced at a flow rate of 160 sccm. The sparger was connected to the inlet of a gas cell that was located in front of the spectrograph. The outlet of the cell was connected to a cold trap (-77 K) and a vacuum pump that maintained the pressure in the cell at 4 Torr. The addition of 6 Torr of either helium or nitrogen to the sparger effluent at the gas cell entrance resulted in comparable quenching of the $O_2\ ^1\Delta_g$ signal. Since the known quenching coefficients for He and N_2 with $O_2\ ^1\Delta_g$ differ by two orders of magnitude,[17] the increased quenching had to be due to a longer residence time in the liquid resulting from the increased backpressure of the added gas.

[17] R. J. Collins, D. Husain, R. J. Donovan, *J. Chem. Soc. Faraday Trans. 2* **1973**, *69*, 145.

[18] J. P. Singh, J. Bachar, D. W. Setser, S. Rosenwachs, *J. Phys. Chem.* **1985**, *89*, 5347.

[19] K. H. Becker, W. Groth, U. Schurath, *Chem. Phys. Lett.* **1971**, *8*, 259.

[20] S. J. Arnold, E. A. Ogryzlo, H. Witzke, *J. Chem. Phys.* **1964**, *40*, 1769.

[21] R. G. O. Thomas, B. A. Thrush, *Proc. R. Soc. London Ser. A* **1977**, *356*, 287.

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